# CO-GROWTH OF 3D SILICON AND 2D SILICON TELLURIDE CRYSTALS: ROLES OF CATALYSTS AND EFFECTS OF CATALYST STABILITIES

by

## Md Shifat Us Sami

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Approved by:

Dr. HaiTao Zhang

Dr. Yong Zhang

Dr. Youxing Chen

Dr. Thomas A. Schmedake

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#### ABSTRACT

## MD SHIFAT US SAMI. Roles of Catalysts and the Effects of Catalyst Stabilities on the Co-Growth of Silicon and Silicon Telluride. (Under the direction of DR. HAITAO ZHANG)

Growth mechanism study is important to achieve high-quality materials growth using more convenient approaches and to realize controlled growth with compositional and structural tunability. In vapor-based deposition, vapor-solid (VS) and vapor-liquid-solid (VLS) processes have been two classic mechanisms for the growth of micro- and nano-scale structures. The VS process is a non-catalyst growth controlled by vapor supersaturation, while the VLS process is a catalyst-assisted growth initiated and guided by eutectic particles. This research reported a cogrowth of three-dimensional (3D) Si crystals with two-dimensional (2D) Si<sub>2</sub>Te<sub>3</sub> crystals and explored its growth mechanism. Chemical vapor deposition (CVD) method has been employed using Te and Si powders as the source materials in the presence of a Cu-coated Si substrate. The growth mechanism study reveals that the Te source plays two different roles in the growth. First, it serves as a reactant which vaporizes and reacts with Si powders to yield 2D Si<sub>2</sub>Te<sub>3</sub> growth via the VS mechanism. A unique "liquid epitaxial growth" was discovered that Te droplets formed prior to the Si<sub>2</sub>Te<sub>3</sub> growth could promote a quasi-epitaxial growth of Si<sub>2</sub>Te<sub>3</sub> crystals on a lattice mismatch substrate. Second, the Te serves as an unstable catalyst for the 3D Si growth. The Si growth is promoted by the synergetic effects of Cu and Te: (1) Cu as a stable catalyst facilitates the reaction of Te vapor species with the Si substrate, forming ternary Te-Cu-Si eutectics; (2) due to the instability of Te, the Te-Cu-Si eutectic particles evaporate and release Si vapor as the precursor for the VS growth of Si crystals. This intermediate process is dubbed as a vapor-liquidvapor (VLV) process which provides a new approach for the material growth with lower growth temperature, lower cost, and higher compatibility for device fabrications.

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# DEDICATION

Dedicated to my parents, to whom I owe everything.

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## LIST OF ABBREVIATIONS

a-Si	Amorphous Silicon
AC	Alternate Current
AFM	Atomic Force Microscopy
APCVD	Atmospheric Pressure Chemical Vapor Deposition
BSE	Backscattered Electrons
СВ	Conduction Band
CNT	Carbon Nanotube
CVD	Chemical Vapor Deposition
CVT	Chemical Vapor Transport
CZ	Czochralski
DC	Direct Current
DTA	Differential Thermal Analysis
EDX	Energy Dispersive X-Ray Spectroscopy
FET	Field effect phototransistor
FFC	Fray-Farthing-Chen
FWHM	Full Width at Half Maximum
FZ	Float-Zone
НСР	Hexagonal Closed-Packed
HT	High-Temperature
IR	Infra-Red
LT	Low-Temperature
MOCVD	Metal-Organic Chemical Vapor Deposition

nc-Si	Nanocrystalline Silicon
NP	Nanoparticle
NT	Nanotube
NW	Nanowire
ОМ	Optical Microscopy
pc-Si	Porous Silicon
PECVD	Plasma-Enhanced Chemical Vapor Deposition
PL	Photoluminescence
RF	Radio Frequency
SEM	Secondary Electron Microscopy
SE	Secondary Electrons
SPM	Scanning Probe Microscopes
ТО	Transverse Optical
UHP	Ultra-High Purity
VB	Valence Band
VLS	Vapor-Liquid-Solid
VLV	Vapor-Liquid-Vapor
VS	Vapor-Solid
VSS	Vapor-Solid-Solid
XRD	X-Ray Diffraction

#### **CHAPTER 1 : INTRODUCTION**

#### 1.1 Background and Motivation

Modern world is rightfully called the Silicon Age as it has paved the corridor for most of human innovation during the last century. Given its unparalleled prevalence in electronics and optical equipment today, spanning from sand to electronic chips, the manufacturing of a silicon product necessitates a comprehensive understanding of its growth process. It is also imperative to understand the formation mechanisms of Si with the help of catalysts, because pure silicon is difficult to produce, and has a very high melting temperature thus making it even more challenging to deposit using vapor-based growth methods at comparatively lower temperatures. The most successful techniques have used silane [1-9], a hazardous [10-12] precursor to produce elemental Si. Research on finding safer alternative, low-temperature, cost-effective methods has been ongoing.

Si is a group IV semiconductor and Te is a group VI metalloid, also known as chalcogen. IV-VI semiconductors are compounds that combine at least one of the elements from group IVA (C, Si, Ge, Sn, Pb) with outer shell electron configuration of ns<sup>2</sup>np<sup>2</sup> and at least one of the elements from group VIA (O, S, Se, Te, Po) aka chalcogens with outer shell electron configuration of ns<sup>2</sup>np<sup>4</sup>. These are some of the most captivating semiconductor materials. A significant number of them have the rock-salt formation , and it is not uncommon for them to undergo structural shifts [13]. Research into IV-VI semiconductors gained renewed momentum in the mid-1960s due to exciting discoveries [14, 15] which was driven by the quest for narrow bandgap semiconductors [13], especially considering the demand for low temperature infra-red (IR) lasers and detectors [13, 16]. Compounds that have received much of the attention in this category since then include PbSnTe [14-16], PbTe [17, 18], SnSe [19], SnTe [18], PbS [20], and GeTe [18], with lead salts having the most technological importance [21]. Others in the IV-VI group with different stoichiometry [22] like,  $Sn_2S_3$  [23], SnSe,  $SnSe_2$ ,  $Sn_2Se_3$  [24],  $Ge_2S_3$  [25] and especially the Si based semiconductors in this group, such as  $Si_2Te_3$  [26-36], were also first introduced around the same time. However, they didn't garner much attention until recently. In the wake of rapid technological advancements over the last century, we've witnessed a continuous evolution of tools, techniques, and methodologies that have paved the way for novel innovations. As these progressions unfold, researchers are turning their attention with reinvigorated enthusiasm to delve deeper into specific structures like  $Si_2Te_3$  that were once overlooked or deemed less significant. This will provide new approaches for the material growth and pave the way for novel device fabrications.

#### 1.1.1 Growth Mechanism for Micro- and Nano-structures

Micro- and nano-structures can be created using top-down methods, which involve patterning and etching followed by oxidation, or through bottom-up approaches, or a combination of both. [37, 38] The methods for synthesis, however, can broadly be grouped into several categories. Vapor-phase growth includes thermal evaporation [39, 40] and other physical vapor deposition (PVD) or sputtering [41], chemical vapor-phase deposition (CVD) [9, 42, 43] metal-organic chemical vapor deposition (MOCVD) [44], arc-discharge [45], laser ablation [46], and others. Also there are solution-phase growth mechanisms [47], the sol-gel process [48], and so on. Of these techniques, thermal evaporation is most frequently used in the study of Si-based micro- and nanostructures. [39]

CVD growth methods [49] typically consist of three fundamental steps: evaporation or sublimation, chemical transportation, and deposition. However, the kinetic processes involved can be intricate. Solid or liquid precursors are first sublimed or evaporated. They are then transported with the carrier gases, during which reactions might occur in the gas phase, forming intermediate reactants and byproducts. Continuous thin films, or other micro- or nano-structures, are formed through surface diffusion and heterogeneous reactions [42]. CVD growth can be carried out in closed tube or in open tubes [16]. The former usually involves transferring chemicals via diffusion or by means of some transporting agent such as a halogen [27] across a sealed ampoule from one end to the other in the presence of a temperature gradient [50]. This technique is primarily used in initial studies of new materials or in cases where the reaction needs to be contained, such as with Al, the fastest-diffusing p-type species in Si [51]. Open tube transport, on the other hand, involves transporting agent/s downstream along with a carrier gas such as H<sub>2</sub> [52-54], N<sub>2</sub> [55] or Ar [16, 51]. The carrier gas flows over a source at a specific temperature and subsequently over a substrate or different nucleation site e.g. tube wall at a different temperature. It is relevant to note another method here in which a gaseous reactant, like SiH<sub>4</sub>, is decomposed on a substrate to produce Si [2, 3, 7-9, 56].

To grasp the importance of CVD methods and highlight some other techniques, it is enough to examine the structure of a basic transistor which is the fundamental building block of modern electronics, enabling amplification and switching. The basic components of a transistor are shown in Fig. 1.1. [56] There are three basic components- the base, emitter, and collector, which are fabricated in combination of some bottom up and some top town techniques. At the bottom, we have a B doped p<sup>-</sup> substrate. On top of it, there is an epitaxial layer of As doped (n-type) Si which is grown using CVD technique. The shaded regions show different layers of SiO<sub>2</sub> isolating the trenches (T) selectively filled with silicon which are both deposited by CVD. The Base (B) and Emitter (E) contact structures are made of polycrystalline Si and are also deposited through CVD. Lithographic techniques are used to create the device's features while ion implantation techniques

are used for dopant distribution. The contacts are made using Al through sputtering or evaporation. The size of the device is less than  $10 \,\mu$ m.

CVD techniques are utilized for various purposes including: (a) the epitaxial growth of n-type Si, doped with As, on a p-type substrate enriched with B; (b) forming multiple layers of conformal SiO<sub>2</sub> (indicated as shaded areas); (c) selectively filling SiO<sub>2</sub>-coated isolation trenches (denoted as T) with Si; (d) creating Base (B) and Emitter (E) contact structures using polycrystalline Si (pc-Si). Device features are defined using lithography, and dopant levels are modified by ion implantation. Al contacts are applied through evaporation or sputtering methods. The spacing between isolation trenches is approximately 5  $\mu$ m, while the vertical dimension is around 3  $\mu$ m.



Figure 1.1: Schematic of a standard bipolar transistor displaying the Collector (C), Base (B), and Emitter (E) zones. [56]

Two classic mechanisms for growing micro- and nano-structures in the final step of the CVD growth process are- vapor-solid (VS) growth [39, 40, 43, 57] which is a non-catalyst growth and vapor-liquid-solid (VLS) [58-64] growth which utilizes a molten catalyst droplet for axial growth. There is also vapor-solid-solid (VSS) [65-67] growth where the catalytic agent for facilitating axial

growth remains a solid, solid-liquid-solid [68, 69] growth where the substrate material tunnels through a liquid metal alloy; solution–liquid–solid [70, 71] growth where semiconductor whiskers are grown through solution phase reactions at low temperatures, supercritical fluid–solid [72] growth where no metal catalyst is required rather an organic solvent such as benzene is used, and etc.

#### 1.1.1.1 Vapor-Solid Growth

In the vapor-solid (VS) process, source vapors are transported to the substrate or nucleation site, where they react and condense in specific temperature zones to form desired structures, governed by vapor supersaturation. This method is simple, cost-effective, and does not require a catalyst to facilitate growth. It can produce various morphologies. However, nucleation is spontaneous [39, 57], and the size and shape of the structure are not controlled, making the process non-selective, although it can be uniform [40] or selectivity can be increased by selective chemical vapor phase etching [73].

Fig. 1.2 provides an example for ZnO. [39] Through thermal evaporation, cation-anion molecules are produced in a stoichiometric ratio (Fig. 1.2c). At lower temperatures, these molecules arrange themselves to form a nucleus on the substrate in a stoichiometric manner, ensuring the local charge and structural symmetry are preserved (Fig. 1.2d). The nucleus growth is continued with the incoming molecules depositing only at the top as the flat sides thermodynamically have lower energy at growth temperature. (Fig. 1.2e). The unevenness of the tip accelerates the gathering of arriving molecules, swiftly creating a nanobelt. (Fig. 1.2f and Fig. 1.2g). Fig. 1.2a and Fig. 1.2b depict the ZnO nanobelts tips. Their growth fronts exhibit a globular appearance, signifying atomic-level roughness. While new molecules might adhere to the growth front or the sides, the smoothness of the lateral surface and enhanced molecular mobility due to

the high temperature cause them to move around and settle at lower energy sites on the growth front. They tend not to attach to the nanobelt's edges due to imbalance in coordination and higher energy. The supersaturation ratio along with the growth temperature measure the nanobelt's cross-sectional size as per crystal growth kinetics.



Figure 1.2: VS growth of ZnO. a, b) The growth fronts/ends of ZnO nanobelts, with no discernible catalytic particles visible at the tips and c-g) Schematic of potential growth mechanisms for the nanobelt formation. [39]

## 1.1.1.2 Vapor-Liquid-Solid Growth

The vapor-liquid-solid (VLS) method for producing single-crystalline 1D semiconductor structures of high quality. Since it was first introduced by Wagner [58] to produce Si microwires in the mid 1960's, this technique has been extensively employed and stands out as the most effective and adaptable approach for growing 1D micro- and nano-structures. In this technique, unlike the VS mechanism, catalyst particles are used to accommodate vapor precursors, form seeds, and guide the growth. It can be a selective growth [74] i.e. controls of site, orientation,

dimension, and morphology of the NWs are made possible. The most common catalyst is Au [58, 74], but a large selections of other metals such as Ti [60], Fe [75], Ag [76], Cu [77], Co [78], Ni [79], Ga [80, 81], Al [81], etc. are also used. Several among them such as Ti, Co, and Ni can form silicides, potentially seeding NWs. [79] It can also be self-catalyzed [57], or even without a metal catalyst e.g. VLS process assisted by sulfur [82].

Fig. 1.3 presents the schematic of Wagner's original and the most simplest example of a typical VLS growth of Si whiskers employing Au as catalyst. [58] In Fig. 1.3a, a tiny droplet of Au-Si alloy is formed on a Si [3] surface through heating a small Au particle at 950°C. A mixture of hydrogen and (SiC<sub>4</sub> + 2H<sub>2</sub>  $\rightleftharpoons$  Si + 4HCI) is introduced as explained by Theuerer [3]. Incoming Si



Figure 1.3: Schematic showing a crystal growth by VLS. a. Initial state featuring a liquid droplet on the substrate and b. Crystal growth process with the droplet at the tip. [58]

atoms enter the Si-Au alloy droplet that serves as a catalyst and get deposited at the solid Si-alloy interface. The process is repeated, and the alloy droplet sits on top of the growing whisker which is shown in Fig. 1.3b. The whiskers grow along <111> direction with sides facing  $(2 \ 1 \ 1)$  but occasionally can also be (211) and (110). The whisker continues to extend in length using this process until either the Au runs out or the growth parameters shift.

Filby [59] described a VLS growth of epitaxial Si layers using a sublimation method via thin alloy zones, depicted in Fig. 1.4. A Si block inside a quartz tube, cooled by water, was subjected to radio frequency (RF) heating to 1300°C, serving as a Si source as well as heater for the Aucoated Si (111) substrate beneath it. With a set gap between them, the substrate's temperature exceeded the eutectic temperature of 370°C, allowing the formation of liquid Au-Si alloy layer. The incoming Si from the source diffused through this alloy, creating a supersaturated solution at the Si-alloy interface. Upon reaching high supersaturation, silicon settled on the substrate.



Figure 1.4: a) Schematic diagram of the Filby & Nielsen's sublimation apparatus for epitaxial growth of Si; b) Si-Au phase diagram; c) Si source and Si substrate with Au-Si alloy layer. [59]

#### 1.1.2 Current Status of Synthesis of Silicon-based Semiconductor materials

Si based semiconductor materials may be of many different forms and compositions. Inorganic Si types include crystalline, amorphous, and porous forms, along with nanoparticles. There are also organic Si compounds, including oligosilanes and polyhedral structures [83]. Production techniques for these materials also vary. For instance, a vacuum-based plasma decomposition method is used for amorphous Si films [83] or cubic Si [84], while specific chemical processes in a container produce polysilanes. However, due to its versatility, CVD is one of the most widely used techniques for producing various Si-based semiconductor materials.

## 1.1.2.1 Review of Synthesis of Silicon

Although it ranks as the second most plentiful element in the Earth's crust [85], Si is almost never found in its pure form. Instead, due to its strong chemical affinity for oxygen, it is primarily found as an oxide, or as a silicate and people have been using compounds of silicon since long before it's discovery as an element. In 1787, Antoine Lavoisier thought of silica to be an oxide and tried to reduce it to its elemental form in a failed attempt. In 1808, Sir Humphry Davy named the element 'silicon' and others soon adopted it. Gay Lussac and Thenard managed to produce an unrefined form of amorphous silicon in 1811, but they were unable to characterize it. The official discovery and isolation of silicon were accomplished by Jöns Jacob Berzelius in 1823 [86] who first reduced K<sub>2</sub>SiF with molten K to get amorphous Si, and also succeeded in producing SiCl<sub>4</sub> in that same year [87]. The crystalline version of silicon was later found by Deville in 1854, 31 years after its initial discovery. [88-90]

Since the early 1960s, elemental Si has been synthesized using CVD. The process begins by converting raw Si into silane, then purifying it through distillation and adsorption. It is then reverted, producing a polysilicon of such quality that additional purification by zone refining is

unnecessary. [91] Silane can be produced in multiple ways. Monosilane, SiH<sub>4</sub>, for instance, is obtained through the hydrolysis of magnesium silicide (Mg<sub>2</sub>Si) using 10% HCl at 50°C [92].

$$Mg_2Si + 4HCl \xrightarrow{50^{\circ}C} 2MgCl_2 + SiH_4$$

Silane can be derived from metallurgical-grade Si through a two-stage method. Initially, at approximately 300°C, Si reacts with HCl to yield trichlorosilane, HSiCl<sub>3</sub> and H<sub>2</sub> gas, according to the given chemical reaction-

$$Si + 3HCl \xrightarrow{300^{\circ}C} HSiCl_3 + H_2$$

F. Weohler [93], was the first to prepare trichlorosilane, employing a technique that still remains in use today for both laboratory and large-scale manufacturing. When trichlorosilane is passed over catalysts like high-Si (approx. 97% Si) ferrosilicon or Si combined with Al [86], nickel, or CuCl, it is subsequently transformed into a silane and silicon tetrachloride, SiCl4, through an intricate sequence of redistribution reactions [94] that can be broadly described as-

$$4HSiCl_3 \xrightarrow{250-400^{\circ}C} SiH_4 + 3SiCl_4$$

There are also other ways of preparing silane. [92]

Initially CVD of Si concentrated on the deposition of single crystal Si at elevated temperatures  $(T \ge 1000^{\circ}C)$ , usually achieved through the thermal decomposition of silane or silicon chlorides denoted as SiH<sub>x</sub>CI<sub>4-x</sub>, where x can be 1, 2, or 3. [56]

The thermal decomposition of silane (SiH<sub>4</sub>) and mono-, di-, and tri-chlorosilanes (SiH<sub>3</sub>Cl, SiH<sub>2</sub>Cl<sub>2</sub>, SiH<sub>3</sub>Cl<sub>3</sub>) with H<sub>2</sub>, in relation to CVD, has been thoroughly examined, including the chemical reactions and the assessment of gas-phase reaction rates. [7] Purnell and Walsh [5] investigated the static vessel pyrolysis of silane using gas chromatography of the reaction product species, first studied by Hogness, Wilson and Johnson in the 1930s. [1] The overall reaction to obtain Si via the thermal decomposition of monosilane can be generally written as: [6]-

$$SiH_4(g) \xrightarrow{>_{600}\circ_{\mathbb{C}}} Si(s) + 2H_2(g)$$

Higher silanes are easier to break down at lower temperatures. Pure silanes can be used to synthesize high purity silicon in this way. [92] Bootsma and Gassen produced Si wires on singlecrystal Si substrates between 550–900°C and 5–100 Torr. [6] Silane is thermally stable at room temperature and starts decomposition at 370°C, but at that temperature the rate is quite slow. Beyond 500°C it decomposes vigorously. [1]

Epitaxial Si layers were grown by reducing silicon tetrachloride (SiCl<sub>4</sub>) using hydrogen at temperatures around 1000°C [2, 3, 58, 95]. Mark identified that the generalized form of the reduction reaction is as follows:

$$SiCl_4 + 2H_2 \rightleftharpoons Si + 4HCl$$

The deposition rate of Si is influenced by various parameters, such as the total gas flow rate, the proportion of SiCl<sub>4</sub> in the H<sub>2</sub> mixture, and the temperature of the Si substrate. [4] This reaction is, however, more complex than it appears, involving the utilization of silane entities. Joyce & Bradley [4] investigated the rates of Silicon deposition in relation to temperature of the substrate and the partial pressure of silane. The findings indicated that the film development required thermal activation, with an activation energy of  $37 \pm 1$  kcal/mole. Eversteyn [96] examined atmospheric pressure chemical vapor deposition (APCVD) of silicon using silane-hydrogen mixtures and observed that the growth rates of the film displayed minimal temperature dependence. This behavior is typical when the rate is controlled by the transport of the reactant to the growth surface. The transport is restricted by the diffusion of the film growth precursors across a boundary layer towards the substrate. [56] Robertson demonstrated that the pyrolysis of silane begins with breakdown on the non-crystalline silicon surface, having an activation energy of 56 kcal/mole, and exhibits minimal dependence on silane pressure. [97]

Growth of Si NWs through VLS growth mechanism has already been mentioned in the previous section. [58] In the CVD process to produce Si NWs, the substrate with metal nanoparticles on its surface is exposed to a Si-containing gas at an elevated temperature. This is typically done under conditions where Si doesn't deposit at a significant rate, such as at temperatures lower than those used for regular Si deposition on Si. For VLS, as mentioned in Wagner's report [58], the catalyst nanoparticles serve as a sink for the incoming Si-containing gas and accelerate its decomposition allowing Si as well as the byproduct atoms to be adsorbed on the surfaces of the nanoparticles. The byproducts desorb into the gas phase and Si moves either through or around the nanoparticle, crystallizing between the nanoparticle and the substrate, leading to a NW formation. Au [58] is the most commonly used metal but others have also been used like Ga [81], Al [81], Cu [98], Sn [99], Ti [60], and etc. The most prevalent Si-containing precursor gases are disilane (Si<sub>2</sub>H<sub>6</sub>), silane (SiH<sub>4</sub>), dichlorosilane (SiH<sub>2</sub>Cl<sub>2</sub>), and silicon tetrachloride (SiCl<sub>4</sub>), listed in descending order of their reactivity; less reactive species require higher temperature to form NWs. [58, 89, 100]

In the VLS process, the Gibbs–Thomson effect establishes a minimum thickness for the wires that can be formed under specific conditions. [95, 100] It was found that, at reduced disilane pressures and elevated temperatures long, untapered Si wires are unattainable using Au catalyst, in the lack of oxygen. Even minimal contact with oxygen limits Au diffusion from the catalyst droplet, enabling its volume to be maintained the same over extended periods, facilitating the formation of uniform thickness wires. This phenomenon occurs with both oxygen carried by gas and oxygen bound to the surface, making the oxygen source nonessential. It was concluded that manipulating oxygen levels during growth could offer a novel method for creating long, uniform thickness NWs, essential for various applications. [101]

Another widely recognized technique is the generation of Si nanocrystals in silane plasmas. [84, 102-107]. Since the early 1990s, many have succeeded in demonstrating the plasma production of silicon nanocrystals. [108-110] A plasma, as described by Langmuir [111], is a partially ionized gas where the Debye radius is notably shorter than its physical size. Plasmaenhanced chemical vapor deposition (PECVD) technique can be used at low temperatures to deposit various forms of Si from silane such as Amorphous (a-Si:H), polymorphous (pm-Si:H), and microcrystalline (μc-Si:H) silicon. In this process, thin layers of hydrogenated amorphous silicon are produced by silane decomposition within a capacitively coupled radio frequency (RF) glow discharge. Considerable endeavors have been dedicated to enhancing the characteristics of the films by adjusting the discharge parameters. A simple schematic by Knights [102] is shown in Fig. 1.5. RF energy is transferred into the gas capacitively using an asymmetrical parallel plate configuration. In this setup, the cathode (C), oscillates with an RF potential and self-biases to a certain negative D.C. potential. For depositions at higher substrate temperatures, the substrates were placed on the anode plate (A). At ambient temperature, both the anode and cathode were



Figure 1.5: Schematic of the plasma-decomposition equipment. [102]

utilized. Deposition speeds of approximately 10Å per second were reached at system pressures of about 0.15 Torr, with a net RF power input of 10 watts or less.

Si nanocrystals for nanoelectronics have been effectively produced using high-frequency PECVD [112] at low temperatures (30-300°C). Thin films were synthesized via RF PECVD with helium and hydrogen diluted silane [113]. Silane plasmas have been used to synthesize Cubic [84, 114], or octahedral [110] shaped nanocrystals of Si, as shown in Fig. 1.6.



Figure 1.6: TEM image of cubic Si nanoparticles. [114]

Silane is a colorless gas that is highly flammable, pyrophoric, and reactive, posing a serious risk of fire and explosion [115]. Breathing it in can irritate the respiratory system, while direct contact can cause severe burns and irritation to the skin and eyes. Prolonged exposure can lead to symptoms like headaches, nausea, and dizziness. [116] Volatile higher silanes ignite spontaneously [117, 118]. Silanes are highly susceptible to hydrolysis and oxidation undergo decomposition through reactions like:

$$SiH_4 \xrightarrow{2O_2} SiO_2 + 2H_2O$$
$$SiH_4 \xrightarrow{4H_2O} Si(OH)_4 + 4H_2$$

Due to these factors, employing silane presents numerous challenges, and scaling up to larger capacities is feasible only with effective management of the associated risks. [9] [10] [12]

The carbothermal (CT) reduction of SiO<sub>2</sub>, a technique developed in the 19th century, remains the primary method in today's silicon industry for use in photovoltaic (PV) energy application purposes. In this method, graphitic carbons act as the reducing agent, converting bulky quartz [119] into crystalline Si within electric arc furnaces.. The overall reactions can be generalized as-

$$SiO_2(s) + 2C(s) \rightarrow Si(l) + 2CO(g)$$

This reaction appears simpler than it is. It involves multiple complex steps and is generally carried out at temperatures ~2000°C. [119, 120] The energy payback time for crystalline solar-grade Si PVs stretches over years, even with cutting edge photovoltaic cell technologies. [9, 121]

When it comes to bulk, single-crystalline, pure Si in the semiconductor and microelectronics industry, there are some well-established methods. [91, 121-124] The most famous one would be the Czochralski (CZ) [122] process of pulling single-crystal, high purity ingots of silicon from a molten pool which is shown in Fig. 1.7 [123]. Within a quartz crucible, feed material is melted. A seed crystal, attached to a rod, is immersed in this molten Si. As the seed is gradually lifted and spun, molten silicon crystallizes onto it, adopting the seed's crystal structure. The resulting large cylindrical silicon ingot, or boule, is then sliced into wafers. Throughout, maintaining precise temperature and pull rate is crucial for ensuring the purity and consistency of the crystal growth. Over 95% of today's bulk Si is grown by the Czochralski method. The remaining Si are primarily grown, or more precisely 'refined', via the float-zone (FZ) method and is used mainly for power electronics and other applications where extremely high purity is required. [91] In the semiconductor industry, nonthermal plasmas are commonly utilized to create and process cubic-shaped silicon nanocrystals, which are essential for nano-electronic devices [84].



Figure 1.7: Czochralski single crystal pulling. [123]

The CT method and the CZ method are honorably mentioned here due to their technological importance. However, this research focuses on vapor growth techniques for Si, as they are essential for the surface-manufacturing of Si-based devices (Si deposited on and growing out from a surface).

Electrodeposition is one of the earliest methods to obtain chemically pure silicon [125]. In 1854, Deville first created crystalline Si by electrodeposition [126]. Recently, Si has been synthesized through electrochemical reduction of SiO<sub>2</sub> in molten salts, notably by employing the FFC Cambridge (FFC: Fray-Farthing-Chen) process [127]. In this method, as presented graphically in Fig. 1.8 [128], SiO<sub>2</sub> is electrochemically reduced to yield pure Si at the electrolyte-SiO<sub>2</sub>-metal trijunction. At this interface, solid SiO<sub>2</sub> is electrochemically transformed into Si, while  $O^{2-}$  ions are moved into the electrolyte and are migrated towards the anode.

$$SiO_2(s) + 4e^- \rightarrow Si(s) + 2O^{2-}(in \ molten \ salt)$$

By this technique, Si nanostructures with controlled morphologies can be produced at relatively low to moderate temperatures (typically 650–900 °C) and the use of risky substances like silane gas is avoided. [128]



Figure 1.8: Electro-reduction of SiO<sub>2</sub>. [128]

In summary, Si is derived from precursor gases via vapor deposition, with Au often serving as the mediating solvent. SiCl<sub>4</sub> mixed with H<sub>2</sub> has been used as Si source, with the reduction, catalyzed by Au/Si alloy at Si wire tips, occurring at around 1000°C. Silane allows for growth at lower temperatures, between 300-600°C, producing polysilicon that doesn't require any further zone refining. However, the hazardous nature of silane poses great challenges. For photovoltaics, the carbothermal process has been the primary method of Si production, but its high temperature requirements (~2000°C) lead to long payback periods. Large single crystals of Si for devices are grown primarily through the CZ or FZ methods. Electro-reduction of SiO<sub>2</sub> serves as another method for synthesizing Si.

### 1.1.2.2 Review of Synthesis of Silicon Telluride

The study of Si<sub>2</sub>Te<sub>3</sub> began way back in the mid-1950s when Weiss and Weiss [26] investigated into the Si-Te system and prepared crystals of SiTe<sub>2</sub>. They heated Si and Te powder at 1050-1070°C in a sealed quartz tube under vacuum for 24 hours and collected the SiTe<sub>2</sub> crystals (red crystalline platelets) forming at the top of the tube. They found the compound to be in the stoichiometric ratio of 9.91% Si and 90.09% Te, density of 4.39 g/cc, and exhibiting a CdI<sub>2</sub>-type [129] crystal structure as they interpreted their XRD analysis data having the hexagonal space group lattice constants of a = 4.28 Å and c = 6.71 Å. A decade later, Rau and Kannewurf [27] reported SiTe<sub>2</sub> single crystals growth using transportation of ingot material in vapor form via a regulated temperature gradient, both in vacuum (1075°C, 48-72 hours), and with iodine vapor present (650°C, 5 days). Lambros followed Rau's growth formula and reported its optical properties [130].

Although most concurred with their observations regarding the compound's physical characteristics, there was prolonged contention concerning its formula. Bailey [28] quenched prereacted samples from 1250°C in air, followed by annealing at 790°C. After a comprehensive DTA and metallographic analysis, he determined that the Si-Te system exists solely as Si<sub>2</sub>Te<sub>3</sub> which others soon [29-32] confirmed. Bailey also developed the phase diagram (Fig. 1.9) indicating that single Si<sub>2</sub>Te<sub>3</sub> crystals, being formed peritectically, can only be practically grown from the vapor phase and cannot be drawn from the melt.

Exsteen [29] used highly pure Si and surplus Te and positioned them at the ends of a 25 cm evacuated quartz ampoule. This was then placed in a horizontal furnace with a temperature range from 700°C (Te) to 900°C (Si). In the central region, sizeable red platelets of SiTe<sub>x</sub>, determined by chemical analysis to have  $x = 1.57 \pm 0.04$ , were formed. Using mass spectrometry, it was revealed


Figure 1.9: Phase diagram of the Si-Te system by Bailey, 1966. [28]

that  $Si_2Te_3$  sublimates incongruently, indicating that the primary particles are  $Te_2$  and SiTe molecules in the vapor phase above crystalline  $Si_2Te_3$ , with molecules of  $SiTe_2$  occurring in negligible quantities.

$$Si_2Te_3(cryst.) \rightarrow (2-x)Si(cryst.) + \left[\frac{3-x}{2}\right]Te_2(vapor) + x SiTe(vapor)$$

Brebrick [30] confirmed that the Si<sub>2</sub>Te<sub>3</sub> phase matches the SiTe<sub>2</sub> that was recognized earlier by others from X-ray powder diffraction patterns. Samples were prepared by heating the elements, ground to less than 1mm particles, in sealed silica tubes under high vacuum between  $10^{-6}$  to  $10^{-7}$ torr, followed by quenching and annealing steps. Samples with a high concentration of Si<sub>2</sub>Te<sub>3</sub> typically had a dark red hue, were malleable, and often produced thin layers when ground. Brebrick scrutinized the relationship between optical density and vapor pressure and identified SiTe(g) and Te<sub>2</sub>(g) as the primary vapor components in the Si-Te system [28, 30]. Importantly, it was found that Te functions as a significant donor in Si, and its solubility seems to be considerably below 1 at.%, which is suggestive of the equilibrium condition between the Si-saturated  $Si_2Te_3(c)$  and pure Si. Another important finding was that the partial pressure of Si-Te was about 40 times smaller than that of Te<sub>2</sub> for the Si-saturated compound, where congruent sublimation would require Te<sub>2</sub> partial to be much smaller than that of Si-Te. This meant that congruent sublimation would be an unlikely option. The lack of congruent sublimation, however, doesn't prevent the vapor growth of Si<sub>2</sub>Te<sub>3</sub>(c) and, in fact, this method is utilized to acquire single crystals of Si<sub>2</sub>Te<sub>3</sub>.

As previously stated, Si<sub>2</sub>Te<sub>3</sub> gained significant attention in the 1960s as the scientific community was holistically looking into the IV-VI semiconductor materials [22, 31]. At that period, significantly more data was accessible for the IV-V1 compounds than for any other semiconductor compound group. While most IV-VI crystals typically exhibited 1:1 or 1:2 stoichiometries, very little about the semiconductors of 2:3 stoichiometry learned and the crystalline Si-Te compound could only be found as Si<sub>2</sub>Te<sub>3</sub>. Subsequently, at the onset of the 1970s, Ploog [32] and Zwick [33] used both the Bridgman technique [131] and the sublimation approach to cultivate sizable single crystals of Si<sub>2</sub>Te<sub>3</sub>. Ploog conducted an in-depth XRD examination, providing the first comprehensive structure of Si<sub>2</sub>Te<sub>3</sub> and found that The unit cell of SiTe<sub>2</sub>, as suggested by Weiss and Weiss [26] should merely serve as a subcell for Si<sub>2</sub>Te<sub>3</sub> with the trigonal constants a = 7.429 Å ( $\approx \sqrt{3} \times 4.289$  Å) and c = 13.471 Å ( $\approx 2 \times 6.735$  Å). Concurrently with Ploog and Zwick, Zeigler [34, 35] heated a stoichiometric mixture in an evacuated and sealed tube inside a resistive furnace between 700-830°C for 5 days and achieved similar Si<sub>2</sub>Te<sub>3</sub> crystals and did optical and electrical measurements.

For at least three important reasons [31] the study of this crystal seemed challenging and made it less appealing for device use. First and foremost, due to its highly hygroscopic nature, it reacts with moisture when exposed to air and decomposes through the following reaction [28]-

$$Si_2Te_3 + 4H_2O \rightarrow 2SiO_2 + 2H_2Te + Te + 2H_2$$

The ruby red Si<sub>2</sub>Te<sub>3</sub> rapidly transitions to black because of the hydrolysis products that is identified on the surface. H<sub>2</sub>Te is easily identified by its distinct smell. Secondly, it seems to be an overly compensated semiconductor that displays p-type conduction across a broad variety of dopants, and its resistivity typically rises significantly with enough dopant concentration. And thirdly, Si<sub>2</sub>Te<sub>3</sub> inherently has a high defect density that results in notably low thermal conductivity values between 1-5 mW/°C-cm and a diminished mobility of less than 1 cm<sup>2</sup>/V sec, along with other atypical traits.

Owing to these issues, later on in the scholarly discourse, Si<sub>2</sub>Te<sub>3</sub>, which was identified in the 1950s, witnessed a decline in attention post the mid-1970s, rendering it somewhat marginalized in subsequent research and was intermittently documented by researchers who followed similar growth methodologies [132, 133]. However, in the meantime, Taketoshi and Andoh [134] verified the existence of SiTe<sub>2</sub> phase and also derived the crystallographic details, finally putting an end to the debate regarding its formula. Multiple investigations have verified that the unit cell of SiTe<sub>2</sub> as proposed by Weiss & Weiss (1953) likely was only a subcell of Si<sub>2</sub>Te<sub>3</sub>. [135]

In 2004, Geim and Novoselov [136] took the world by surprise with their discovery of graphene. Researchers around the world started looking into graphene and other 2D materials and, down the line, especially since in the past decade, Si<sub>2</sub>Te<sub>3</sub> nanostructures have been revisited as potential components for Si-backed devices because of their distinct structural differences and newly found promise as a 2D layered material. [36, 137-158]

Koski's lab [36, 137, 138] at the Brown University first employed an open tube vapor deposition system for synthesis of Si<sub>2</sub>Te<sub>3</sub>. Keuleyan [36] successfully accomplished the growth of Si<sub>2</sub>Te<sub>3</sub> nanoribbons and nanoplates through VLS mechanism. They replicated Peng's [80] setup and utilized a 1-inch quartz tube inside a 12-inch furnace for Si<sub>2</sub>Te<sub>3</sub> growth as shown in Fig. 1.10. The tube was put under vacuum (0.1 Torr) and was flushed with Ar before adjusting pressure (15 Torr) and gas flow (15 SCCM). The gas flow line and the tube junction were equipped with a filter designed to eliminate oxygen to further reduce the oxygen impurities from the flow. For the nanoribbons and vertical nanoplate growths, high purity Te (30 mesh, 100 mg) and high purity Si (325 mesh, 100mg) powders were positioned upstream at designated locations, and deposition substrates like silicon (100), fused quartz, or sapphire were positioned downstream, targeting temperatures around 400-680 °C. It was then heated to 800 °C at a speed of 60 °C/min. At this heat, Si didn't vaporize significantly, but could react with Te<sub>2</sub> vapor, leading to Si-Te formation. On the substrate, the nanoribbons (Fig. 1.11a) grew towards the high temperature region starting at around ~680 °C, where Te spheres formed through evaporation and deposition, which afterward served as catalyst for the VLS growth of nanoribbons. Excess tellurium resulted in specific growth



Figure 1.10: (a) Arrangement for the synthesis of  $Si_2Te_3$  nanoribbons and vertically oriented nanoplates and (b) Configuration for growing planar nanoplates by seeding the substrate with Te. [36]



Figure 1.11: Nanostructures of  $Si_2Te_3$  grown through CVD technique: a) nanoribbons, b) vertical nanoplates, and c) flat nanoplate. [36]

patterns. Once reaching 800 °C, the setup was cooled rapidly. The growth process was completed in under 30 minutes, and the distinct red-colored Si<sub>2</sub>Te<sub>3</sub> crystals were immediately visible. Raman spectra provided evidence of the presence of Si, Te, and Si<sub>2</sub>Te<sub>3</sub> in the Te catalyst and in the nanoribbons. The vertical plates growth (Fig. 1.11b) was observed towards the lower temperature region starting at around ~650 °C. This growth mode showed strong crystallographic orientation implying a significant interaction between the substrate and a specific crystal face. Given its unique morphology, it is believed these plates arise from VS growth influenced by crystal orientation. For the horizontal nanoplates growth (Fig. 1.11c), extra Te source were placed at 850°C, Due to low melting point, Te evaporated first and condensed onto the substrate forming Te pools (100-300 µm across) which was verified through optical microscope and SEM images. Large, flat, hexagonal shaped single crystals of Si<sub>2</sub>Te<sub>3</sub> that reach 1–150 µm across were grown from this pool mimicking the epitaxial Si growth through VLS mechanism as Filby reported [59]. To prevent decomposition from hydrolysis, samples were swiftly moved and stored in a N<sub>2</sub> glovebox. Wang [137], and Johnson [138], also from Koski's lab, followed the same growth method as they doped the structure with Ge and Mn, respectively to see the substitutional doping effect on the optical properties of Si<sub>2</sub>Te<sub>3</sub> nanoplates.

In recent times, besides Koski's group, Shen and Cui's group at the University of Memphis, Tennesse investigated in a \$393K project funded by NASA. [139-147] Their team integrated firstprinciples calculations for theoretical analysis along with hands-on synthesis and characterization in order to deeply understand how changes in the 2D structure of Si<sub>2</sub>Te<sub>3</sub> influence its properties. They investigate different strain and doping optimization techniques. Wu [139, 140], an author from Shen and Cui's group mentioned of using the same instrumental setup for CVD growth of Si<sub>2</sub>Te<sub>3</sub> as Koski's group [36, 137, 138] with a few changes. A 40–80 nm thick coating of Au was used as the catalyst. N<sub>2</sub> was used as the carrier gas, and the flow rate was set at 15 SCCM. Source powders (Te and Si) were placed upstream in a ceramic crucible and the coated substrate was placed downstream. The system was evacuated prior to growth and the growth was carried out at a pressure of 9.12 Torr. A slower heating rate of 20 °C/min was used to heat the furnace up to 850  $^{\circ}$ C, and then cooled down after growth being carried out between 550 to 650  $^{\circ}$ C for 3–5 mins. Accordingly, Si<sub>2</sub>Te<sub>3</sub> nanostructures like nanotapers were formed along with the NWs and nanoplates, a result somewhat different from what Keuleyan [36] reported, This is believed to be primarily due to a different catalyst coating, i.e. Au, on the substrate. Fig. 1.12 displays the conelike structures of Si<sub>2</sub>Te<sub>3</sub> that have a broad base measuring approximately 3  $\mu$ m in diameter and taper to pointed ends. These formed in the region at 580 °C with a growth duration of around 4



Figure 1.12: SEM images of -Si<sub>2</sub>Te<sub>3</sub> (a) nanotapers and (b) NWs grown at different temperatures. [140]

minutes. The circular caps atop each structure can be clearly identified as Au catalysts suggesting VLS growth mechanism. The author suggested that this likely means the rate of growth at the structure's tip outpaces that in the horizontal direction, possibly because of the catalysts' presence. However, this could also signify progressive integration of excess NW species within the droplet, as evidenced by experimental proofs. [64] The ideal composition of droplet constituents seems to be of vital importance for VLS NW development, especially for NW nucleation processes that utilizes a foreign element catalytic agent (FECA).

Fig. 1.13a displays the SEM image of specific Si<sub>2</sub>Te<sub>3</sub> structures where NWs emerge from tapered pedestals. The author characterizes the growth mechanism as a mix of VS and VLS, as depicted in the schematic of Fig. 1.13b. This is thought to result from shifts in the Si/Te ratio in the vapor phase over time and with temperature changes. Dayeh's research [159] on the VLS growth of InAs NWs indicated that the growth mode transitioned from VS to VLS as the V/III ratio decreased. It's plausible that, at reduced substrate temperatures, VS is the preferred growth mechanism because of the elevated Te/Si ratio. This is attributed to Te's high vapor pressure, causing a shift towards VS growth over VLS. However, as the temperature increases, leading to a reduced Te/Si ratio, NWs begin to grow on the top. The tapered growth can be credited to factors like surface free energy and the wettability of the initial liquid nuclei responsible for growth. When



Figure 1.13: a) SEM image and b) schematic diagram of growth mechanism of a Si<sub>2</sub>Te<sub>3</sub>. [140]

Si dissolves in liquid metal catalyst droplets like Ni, Au, Cu, and Pt, it has been demonstrated to reduce the metals' wettability on the surface of Si. This leads to a significant rise in the contact angle, which in turn results in tapered growth [160-162]. However, as the Te/Si ratio drops to a specific threshold, the VS growth method gives way to the VLS mode. The tapered Si<sub>2</sub>Te<sub>3</sub> structure consists of nanoplates that are generally smaller in size and typically constrained by the catalysts.

Fig. 1.14 displays flat Si<sub>2</sub>Te<sub>3</sub> microplates that, as Keuleyan reported [36], were observed to grow at varying temperatures using the VLS mechanism. Meanwhile, vertical and inclined plates seemed to have formed via the VS method (Fig. 1.15). The growth pattern is further detailed in Keuleyan's report [36]. EDX analysis of both the NWs and nanoplates confirmed the 2:3 ratio for



Figure 1.14: Growth process of Si<sub>2</sub>Te<sub>3</sub> microplates: a–c) SEM images and d–f) Schematic. [140]



Figure 1.15: SEM images of a) vertical and b) inclined Si<sub>2</sub>Te<sub>3</sub> nanoplates. [140]

Si:Te, as one would anticipate for  $Si_2Te_3$ . Some theoretical studies have been reported [144, 148, 157] recently that is beyond the scope of this thesis and there are others who reported on device applications or optoelectronic performances [137, 154, 163].

Among the most recent reports, bulk crystals and thin films of Si<sub>2</sub>Te<sub>3</sub> were grown by Hathaway [155, 156] using a custom CVD system as shown in Fig. 1.16. Inside a 600 mm-length Across furnace, a 1-inch quartz tube was placed within a 2-inch quartz tube. This inner tube conserves evaporated source materials, minimizing the needed quantity for sample growth. A sealed quartz tube, 7 cm-long and filled with Si and Te powders, was positioned in the furnace's center, guiding the evaporated materials toward a substrate located 5 cm from its open end. The system was evacuated and flooded with 80 sccm N<sub>2</sub>, achieving a pressure of around 5000 mTorr. The temperature was raised to 850 °C in two steps, maintained for 5 minutes, followed by fast or slowly cooling to room temperature. To produce either bulk crystals or thin films, source material quantity and cooling duration were varied. Thin films required around 80 mg of Ti and 60 mg of Si, cooled swiftly to room temperature by unsealing and venting the furnace. Conversely, 300 mg of Te and 200 mg of silicon are used for bulk crystals, and the sample cools gradually without opening the furnace. Thin films take approximately 1.5 hours to grow, while bulk crystals need about 4.5 hours. A thorough and multifaceted analysis of the Si<sub>2</sub>Te<sub>3</sub> degradation processes was conducted using optical assessments and various characterization methods.



Figure 1.16: Custom CVD setup for the deposition of Si<sub>2</sub>Te<sub>3</sub> thin films and bulk crystals. [155]

In the literature, only a few investigations have been documented regarding the growth of amorphous silicon telluride thin films through magnetron sputtering from a polycrystalline  $Si_2Te_3$  target. [31, 152] These films typically adopt a chemical composition represented as SiTe or  $Si_xTe_{1-x}$ . Contrary to crystalline  $Si_2Te_3$ , the amorphous variant appears to exhibit minimal decomposition when exposed to air. Remarkably, some bulk samples of this material have been successfully machined and polished, even employing water as a coolant.

To summarize, before the discovery of graphene, techniques like simple evaporation or chemical vapor transport (CVT) were employed to grow crystalline  $Si_2Te_3$ . This process necessitated sealed evacuated ampules and spanned weeks for growth. While there was consensus on its physical properties, its chemical formula has been a topic of serious debate for decades. In the past decade, as 2D materials brought renewed potential to the scientific community, researchers have revisited  $Si_2Te_3$  to examine its structure and properties. CVD has emerged as a favored method to grow and analyze this distinct 2D, layered semiconductor material.

# 1.2 Scope of this Dissertation

This dissertation primarily focuses on the synthesis of crystalline  $Si_2Te_3$  using the CVD technique and includes an intriguing aspect of the serendipitous discovery of 3D Si crystal growth (particles) under certain conditions. This unexpected finding adds a novel dimension to the research and potentially broadens its scope and implications.

1.2.1 Growth Mechanism study of 3D Silicon and 2D Silicon Telluride Structures

The foundational element of this study is an extensive literature review. This involves a critical analysis of existing methodologies and outcomes of  $Si_2Te_3$  synthesis. The aim is to identify potential areas of innovation and improvement. This review provides a comprehensive backdrop against which this research is conducted.

Central to the dissertation is the exploration of catalysts' roles, specifically Cu and Au, in the growth process of Si<sub>2</sub>Te<sub>3</sub>. In our group's previous study [62], thorough investigation was made using Au as catalyst. However, this investigation was primarily focused on comprehending how these catalysts, especially Cu influence the crystalline structure and quality of the material. Cu is also a common catalyst for Si growth like Au. They have similar eutectic forming properties with Si and Te. From the prior work on Au, we tested whether Cu would behave similarly and whether there were any differences. New results were subsequently discovered. Cu is also much cheaper, and more importantly, it has a large diffusion rate in Si [164]. The serendipitous growth of silicon, observed during certain experimental conditions, was thoroughly examined to understand its underlying mechanisms and implications. This aspect of the research opens new avenues for inquiry and may have significant implications for the synthesis of other materials. Throughout the research process, adherence to safety protocols and good chemical handling practices were made a priority. The importance of maintaining a safe and controlled research environment is paramount, particularly with regard to the unexpected findings.

Characterization of the synthesized Si<sub>2</sub>Te<sub>3</sub>, and the inadvertently grown Si, is meticulously carried out using standard tools such as SEM in conjunction with EDX, Raman, and XRD. These characterizations are crucial for understanding the structural, morphological, and compositional aspects of the materials produced. It should be noted that the scope of this dissertation does not extend to computational studies of Si<sub>2</sub>Te<sub>3</sub> synthesis and is confined to experimental investigation.

In summary, this dissertation not only contributes to the understanding of  $Si_2Te_3$  synthesis via CVD but also introduces an unexpected dimension in the form of silicon growth, thus offering a unique contribution to the field of semiconductor materials and potentially influencing future research directions.

#### 1.2.2 Structure of this Dissertation

The chapters in this dissertation are structured in such a way that each address distinct aspects of the research. An extensive literature review, presented earlier in this chapter, covers VS and VLS growth mechanisms and chronicles the development and current methodologies in the synthesis of Si and Si<sub>2</sub>Te<sub>3</sub>. This review is essential in providing crucial background information and setting the context for subsequent research.

The experimental setup, including the custom-made CVD chamber with its major components and their functionalities, is described in detail in the second chapter. The growth process, from the initial steps of raw materials processing and substrate preparation to the specifics of growth parameters and experimental design, is elaborated on in the following sections. The chapter is then concluded with a brief overview of the characterization techniques employed in the study.

In the third chapter, the properties of Si and  $Si_2Te_3$  are thoroughly examined: their crystal structures are discussed, and their physical, optical, and electrical properties are listed, providing essential information pertinent to the research. The experimental methodologies for different setups are outlined, and the corresponding results are presented and analyzed in detail.

The focus of the fourth chapter is the mechanism study for  $Si_2Te_3$  growth. A series of additional experiments are conducted, aimed at confirming theoretical assumptions and adding significant value to the overall research.

In the concluding chapter, the key findings of the thesis are summarized and potential directions for future research are suggested. Additional studies are highlighted, and a forecast of the potential outcomes of this research, based on these developments, is presented.

An appendix is included that provides supplementary information, offering additional context and supporting the main chapters to ensure a comprehensive presentation of the research.

#### CHAPTER 2 : EXPERIMENTAL TOOLS

A detailed description of the home-made CVD system that was used in this research is presented in this chapter. The growth process, from the initial steps of raw materials processing and substrate preparation to the specifics of growth parameters and experimental design, is elaborated on in the following sections. General characterization tools used in this study are briefly introduced. The details provided are enough for skilled material scientists to replicate these experiments, with added context for clarity.

# 2.1 Growth System: Home-made Chemical Vapor Deposition System

A home-made hot-wall CVD system was used in this project. Similar CVD systems have been used for the nanostructures growth of tungsten oxide [165], sodium tungsten oxide [43], titanium oxide [165, 166], boron [167], borides [168], silicon oxide [62], Molybdenum Oxide [67], and MoO<sub>3</sub> [169]. The system can be divided into three sections- the gas supplies and flow controllers, the furnace and reaction chamber, and the vacuum system as shown in Fig. 2.1 below. A schematic is provided showing the connections in Fig. 2.2.



Figure 2.1: Photograph of the home-made CVD system.



Figure 2.2: Schematic of the home-made CVD system.

## 2.1.1 Gas supplies and flow controllers

UHP (ultra-high purity) Ar was used as carrier gas and UHP  $H_2$  was used to provide a reduction growth environment to prevent possible oxidation form residual oxygen throughout this research. [151] Each of the two gas cylinders was equipped with Mass-Trak flow regulators (Sierra Instruments, Inc.) which helped to maintain a steady flow of 20 sccm Ar and 5 sccm  $H_2$  for typical growths.

Argon is used as the background carrier gas, while H<sub>2</sub> is employed as a reducing agent to avert oxidation. [52-54] A faster deposition rate is achieved using H<sub>2</sub> compared to Ar or N<sub>2</sub>, and it is also helpful in enhancing the kinetics and thermodynamics of the growth process. H<sub>2</sub> is advantageous for maintaining higher temperature and better heat distribution, whereas steep thermal gradients can be produced by Ar. [170] The dynamics of carrier gas flow in the CVD reaction tube under various conditions, however, have been relatively less examined. [171, 172] Using Ar or N<sub>2</sub>, having higher molecular weights than H<sub>2</sub> or He, has advantages in terms of increased vacuum pump efficiency.

## 2.1.2 Furnace and Reaction chamber

The reaction chamber is made of a 1-inch diameter fused silica tube (Quartz Sci, Inc.) housed in a hot-wall furnace, as shown in Fig. 2.1. Two semi-cylindrical shaped ceramic fiber heaters (Watlow, Inc.), with power density of 0.8 - 4.6 W cm<sup>-2</sup> (60V, 275W), construct the furnace. The tube is connected to the gas supplies through the flow controllers on one end and to a mechanical vacuum pump through the pressure controller on the other. The furnace is 8 inches long, including 1-inch cooling zone on each side, leaving the heating zone exactly 6 inches long. The temperature profile at a set point of 850°C, the typical growth temperature, along with materials loaded into specific positions for visualization, is shown in Fig. 2.3. The central region of the furnace maintains



Figure 2.3: Temperature profile inside home-made CVD chamber in ambient environment.

a nearly uniform temperature, which gradually reduces towards the sides and rapidly decreases in the cooling zones. In this study, the upstream-edge of the furnace is designated as the 0-inch position, with values increasing positively towards the downstream side. The power delivery and heating/cooling cycles are controlled by the Temperature and Process Controller (Omega CN8500 Series 1/16 DIN) and a Variac. Besides temperature, the other controllable parameters of this CVD system include gas flow rate, position and amount of the source material, type and location of the substrate, and the actual pressure of the CVD chamber. The functional capacity of the home-made CVD system is outlined in Table 1 below.

		Unit	Range/location	Resolution
Temperature		°C	$RT - 1100\ ^{\circ}C$	±1
Pressure		Torr	8 mTorr – 760 1 atm	Associated to flow
Flow	Ar	Sccm	0 - 100	1
	$H_2$	Sccm	0 – 30	0.1
Location (From left)	Source	Inch	0 – 8	±0.05
	Substrate	Inch	0 - 8	±0.05

Table 1: Home-made CVD operational parameters.

In a typical growth process, source materials are placed at upstream locations, with Te at the 1-inch mark and Si at 4 inches, each on separate quartz boats. The growth substrate is positioned on the same boat as Si at the 7-inch position, while the catalyst-coated or control specimen is usually located at the 5-inch spot. During heating, Te begins to evaporate first due to its low sublimation point, and as the chamber reaches the target temperature, it is transported by the carrier gas and may or may not react with Si and the catalyst or control specimen. The reaction or growth species are then conveyed by the carrier gas, bombarding onto the substrate and the chamber wall as they approach the cooling zone. Some of these species will be adsorbed by the substrate, transforming into adatoms under favorable equilibrium conditions. Meanwhile, others may persist

as gas molecules, either awaiting further reactions or being swept downstream by the vacuum, a rather complicated process governed by thermodynamic principles which will be elaborated upon in the Chapters 3 and 4.

## 2.1.3 Vacuum system

In the downstream the vacuum section was equipped with a rotary vane pump (Aclatel Pascal 2010SD) connected to the CVD chamber through an automated throttle pressure control valve (Model type 653B) which was connected to an MKS pressure controller system (600 Series) and it was possible to maintain the system pressure from several mTorr to several hundred Torr. A diaphragm manometer (Vacuum Research) was used in conjunction with a pressure guage (MKS 626A13TQE) to monitor the pressure inside the growth chamber.

# 2.2 Growth Procedure

The preparation of raw materials and substrates is crucial for the successful growth of semiconductors, primarily for two reasons. First, properly prepared materials minimize contamination and defects, which are essential for achieving the desired electrical and optical properties in semiconductors. Second, the presence of extraneous elements can alter the crystallization process, potentially leading to atypical crystal structures. Such deviations can result in misleading interpretations of the underlying mechanisms or the functional properties of the material. Equally important is the precise control of growth parameters; consistency here is key. Even a subtle change can cause significant shifts in the resultant product. In short, meticulous substrate preparation and control at every step lay the foundation for uniform crystal growth, which is essential for consistent semiconductor performance and reliability.

## 2.2.1 Raw Materials

The main source materials used in this study were pure Si powder (99%, -325 mesh, Aldrich), pure Te powder (99.8%, 200 mesh, Aldrich), and pure Cu powder (99%, 100 mesh, Aldrich). When necessary, powders were mixed in a glass vial using a LP Vortex Mixer (Fisher Scientific) at 2000 rpm for 2 minutes. Raw materials were measured on a scale, with measurements often recorded as approximate. The Te powder was loaded on one end of a smaller quartz boat, measuring  $61\times15\times7$  mm. The Si and/or Cu powders were typically loaded separately on one end of another larger quartz boat, measuring  $114\times18\times8.5$  mm. The substrates were loaded on the same boat as the latter, typically positioned 1, 2, or 3 inches away from the powder. (Fig. 2.4)



Figure 2.4: Raw materials and substrates.

## 2.2.2 Substrate Preparation

In this study, two types of substrates were used- bare Si (111) substrates, and Si (100) substrates with thermal SiO<sub>2</sub> layers of 300nm, 500nm, or 1 $\mu$ m thickness.

The bare Si (111) substrates are used as additional Si source and chosen because of its availability in stock at the time. No particular crystallographic direction was given a priority. The thermal oxide coating on the growth substrate allowed deposition without unwanted chemical interaction of the incoming growth species with the substrate. Each rectangular substrate was cut from 100 mm wafers (University Wafer Inc.) and measured 24 mm by 8 mm.

## 2.2.2.1 Plasma cleaning

Each bare substrate was cleaned by ultrasonication (Branson 1510R-MTH) in acetone followed by reagent alcohol, for approximately 15 minutes, and then subsequently blow dried using N<sub>2</sub> gas. Ultrasonication enhances the cleaning process by creating high-frequency sound waves that produce cavitation bubbles in the liquid. These bubbles implode with great force upon contact with the substrate surface, effectively dislodging contaminants. Acetone is a powerful organic solvent that is highly effective at dissolving organic contaminants like oils, greases, and some types of adhesives. Reagent alcohol, typically a mixture of ethanol, isopropanol, and methanol, is used after acetone for further cleaning. It is effective at removing any remaining organic residues that acetone might have missed. The combined mechanical action of ultrasonication and the sequential use of these solvents with their solvent properties work together in removing these organic compounds from the substrate surface. The quick drying action of the nitrogen blow shortens the evaporation time of the residual liquid, thereby helping to prevent airborne particles from being adsorbed by this liquid and subsequently settling on the surface.

The ultrasonically cleaned substrates are then plasma cleaned [173-175] using oxygen at low pressure (Kurt J. Lesker, Plasma-Preen II 862). The cleaning process is carried out at 600-800 mTorr for 2 minutes. There are several advantages that plasma cleaning offers. Oxygen plasma is highly effective in removing organic residues from silicon substrates at the nanometer level. The reactive oxygen species generated in the plasma ( $e^-$ ,  $O^+$ ,  $O_2^+$ ,  $O^{2-}$ ) remove any residual organic compound by reacting with them and transforming them into volatile molecules like CO, CO<sub>2</sub> and H<sub>2</sub>O. Additionally, the surface energy of Si substrates can be increased by plasma treatment, making them more hydrophilic. This enhanced wettability and improved adhesion properties of

the Si substrate, ensures that layers added later adhere properly and uniformly which is beneficial for subsequent processes like coating, bonding, or photoresist application.

#### 2.2.2.2 Sputter coating

For catalyst-assisted growths, clean Si (111) substrates were coated with a thin layer of metal (Cu or Au) using a magnetron sputtering (Denton Vacuum Desk IV) system (Fig. 2.5b-e).

When it comes to depositing thin films, sputter deposition has been a widely recognized Physical Vapor Deposition (PVD) technique. A solid target is usually used as the film-forming material source (cathode). The process involves momentum transfer from high-energy particles, usually ions of an inert noble gas such as Ar, to the target's atoms. An external power source, such as DC or RF, ionizes neutral Argon atoms, resulting in the production of a glow discharge, also known as plasma. A cathode sheath placed next to the source (i.e. the target or the cathode) causes the ionized particles to bombard on the cathode surface in high vacuum, dislodging target atoms via momentum transfer, which then diffuses through the vacuum chamber and gets deposited onto the substrate, creating a thin film. In the DC magnetron sputtering system, shown in Fig. 2.5a [176], a permanent magnet is positioned behind the cathode target which creates magnetic field lines that traverse the cathode plate inward and outward, forming a glowing, high-density plasma ring discharge (shaded region). This ring, having a width 'w' and an average radius 'R', floats beneath the cathode while sputtering takes place in a corresponding track on the cathode.

A great advantage of this method is that thin films created this way usually has higher density, smaller grain size, and better adhesion, closely resembling bulk material properties, unlike those from thermal evaporation. [177, 178] It is often used for facilitating SEM observation.





Figure 2.5: a) Schematic showing planar magnetron discharge; reproduced from Lieberman. [175] b) Denton Vacuum sputter coating instrument; c) target (cathode); d) substrate/base (anode); e) glow discharge as observed through the viewing window during growth.

# 2.2.3 Growth Parameters

Unless specified otherwise, typical parameters of growth reaction are listed in table below.

Source powder	Te	weight	~250 mg	amount chosen to ensure supply for 1-hour growth	
	Si	weight	~60 mg	initial amount	
Substrates	SiO <sub>2</sub> /Si	thermal oxide coating thickness	300 nm 500 nm 1μm	cut to 25 mm × 8 mm rectangles from 100mm disk	
	Si (111)	w/ or w/o catalyst		cut to 25 mm × 8 mm rectangles from 100mm disk	
Metal catalyst (as powder)	Cu	weight	~127 mg	1:2 molar ratio with ~60 mg Si	
Metal catalyst	Cu	sputter coating thickness	18 nm		
substrate	Au	sputter coating thickness	10 nm		
	Ar	gas flow rate	20 sccm		
Gas now	$H_2$	gas flow rate	5 sccm		
		Ramp time	15 mins	1	
TT - 1		Ramp rate	55 °C/min	temperature	
Heating and cooling cycle for growth		Temperature setpoint	850 °C		
for growth		Growth time	60 mins		
		Cooling rate	≤14 °C/min	time	
		Ramp time	15 mins		
		Ramp rate	55 °C/min	temperature	
for annealing		Annealing temperature	850 °C		
for annearing		Annealing time	30 mins		
		Cooling rate	≤14 °C/min	time	
Growth atmosphere		Pressure	100 Torr	Pressure is initially set to 10 Torr and then stopped. Pressure is maintained once it reaches 100 Torr.	

Table 2: Typical Growth Parameters.

## 2.3 Experimental Design

In typical growths processes, approx. 250g of Te powder was loaded upstream on the shorter quartz boat at the 1-inch position (approx.  $670^{\circ}$ C) as the source material. The other source material, approx. 60 g of Si powder, was loaded at the 4-inch position on the longer quartz boat (approx. 850°C, which is also the center location of the reaction chamber). The same boat also hosted the growth substrates. One, two, or three substrates were placed downstream of both powders at predetermined locations (5-inch position at ~838°C, 6-inch position at ~808°C, 7-inch position at ~677°C) as shown in Fig. 2.6.



Figure 2.6: Experimental setup for the CVD.

After loading the sample, it was ensured that all connections to the reaction chamber were properly sealed. The chamber was then evacuated to a vacuum pressure below approx. 10 mTorr. 20 sccm Ar was introduced as a carrier gas for vapor precursor transport. Following the stabilization of the Ar flow using the mass flow meter, 5 sccm of H<sub>2</sub> was added as a reducing gas to prevent potential oxidation. Once both Ar and H<sub>2</sub> gas flows had stabilized, the furnace was heated to 850°C in 15 minutes ramp time, maintaining that temperature for a growth time of 60 minutes. At the start of the temperature ramp, the initial system pressure was set to 10 Torr with the stabilized flow of Ar and H<sub>2</sub>. Subsequently, the gate was stopped to allow the pressure to rise as more vapor species were introduced through the sublimation/evaporation of the source material.

As the temperature rose, Te began sublimating causing the pressure to increase. Once the pressure reached the target of 100 Torr during the heating cycle, it was maintained at this level using the automatic pressure control system. After 60 minutes of growth at 850°C, heating was stopped, and the system was left to cool down gradually to ambient temperature over a few hours. Once cooled, the samples were immediately placed into airtight vials with Indicating Desiccant Absorbent (Drierite 23005-EA, 8-Mesh) to prevent decomposition.

In control experiments, different growth times ranging from 0, 15, to 60 minutes were used to study growth evolution. For mechanism studies, growth experiments were conducted with the addition of various catalysts (e.g., Cu, and Au), and annealing experiments were performed.

## 2.4 Characterization tools

Although the samples were kept in sealed containers, the shelf life of  $Si_2Te_3$  before decomposition is not long and the samples would turn from reddish to dark gray within a few weeks. Therefore, it was essential that the characterizations were carried out ideally on freshly grown samples.

## 2.4.1 Optical Microscopy (OM)

Bulk sample panoramic images were captured using an optical microscope (Olympus DSX 1000). Individual images were digitally stitched together to form a rectangular panoramic view (24 x 9) of the sample, revealing zones that are visible to the naked eye.

#### 2.4.2 Scanning Electron Microscopy (SEM)

In SEM [179-181], a beam of high-energy electrons (ranging from 0.1 to 30 keV) is focused onto a specimen. This electron beam, created by an electron source and shaped using lenses and apertures, scans the sample in a raster pattern. As the beam hits the sample, various types of radiation are produced within the interaction volume due to inelastic scattering that can provide valuable signals for various purposes, such as imaging and chemical analysis. Two main types of emitted electrons are: backscattered electrons (BSEs), which retain most of their energy, and secondary electrons (SEs), which are emitted from the atoms of the sample with low energy (0–50 eV). These electrons are detected to form an image, with each point on the specimen corresponding to a pixel on the display screen. Since BSEs retain most of their energies, they are strongly contingent on the material's atomic number, Z, allowing for compositional analysis. SEs on the other hand, having low energy, are mostly reabsorbed if they originate from deeper within the specimen (Fig. 2.7). Only those near the surface manage to escape, making SE images strongly sensitive to surface topography. Other emissions, including X-rays and Auger electrons, also emerge from the specimen and have specific applications. The SEM operates in a high vacuum to minimize unwanted electron scattering. To avoid the accumulation of charge, insulating samples are typically covered with a conductive coating.

The SEM (JEOL JSM-6480) used in this research, utilizes a tungsten filament source, heated to approximately 2800 K, with an acceleration voltage of up to 30 kV and it is equipped with an



Figure 2.7: a) Production of secondary and backscattered electrons. b) The interaction zone and areas from where secondary electrons, backscattered electrons, and X-rays can be obtained. Image from Goodhew. [180]

EDX (INCA 7573-M) system. Maximum resolution that can be achieved is 10 nm. Both SE and BSE images were captured at a 20 kV acceleration voltage, with an approximate working distance of 10mm and a spot size around 30. SE images were used to examine sample morphology, while BSE images highlighted compositional variations.

## 2.4.3 Energy Dispersive X-Ray Spectroscopy (EDS)

X-ray emission during EM comes from inner shell bandgap transitions of the constituent atoms, a process called cathodoluminescence, which allows for elemental and chemical analysis in SEM and TEM. It is possible to analyze microscopic volumes in specimens through focusing the electron probe on a very small area, hence the term microanalysis. However, the characteristic X-rays are generated not from the top region but from a region beneath the sample's surface, as shown in Fig. 2.8a. When examining the microscopic section of a bulk sample in SEM, the EDS signals originate from a region significantly larger than the diameter of the probe. The lighter the elements are, the larger the analyzing area becomes. [182] For this reason, one must carefully



Figure 2.8: a) Analogy of X-ray generation regions with samples of varying mass densities ( $\rho = 3$  gcm<sup>-3</sup> for the left and 10gcm<sup>-3</sup> for the right samples. b) Possible X-Ray detection interference arising from low take-off angle. [182]

select an area on the sample's surface to ensure uniform distribution of elements in the X-ray production area. Another issue is the possible overlap of K and L lines from lighter and heavier elements, respectively, causing uncertainty. Preassigning potential elements during analysis in such cases can be helpful. Take-off angle can also potentially interfere with the X-ray detection in SEM (Fig. 2.8b). To prevent this, the surface should be flat and positioned to allow the electron beam to enter perpendicularly.

The EDS system integrated with the SEM (INCA by Oxford Instruments) used in this research features an X-ray detector (10 mm<sup>2</sup> Si, cooled by liquid N<sub>2</sub>) and a super-thin window, allowing for the detection of light elements like B. Similar to the SEM and BSE imaging utilized in this study, a 10 mm working distance for a 20 kV acceleration voltage, and a 60-second acquisition time were used. The spot size was adjusted to maintain a deadtime of approximately 30-40%.

## 2.4.4 X-ray Diffraction (XRD)

XRD is a technique for studying the crystalline structure of materials. When X-rays strike a crystal, they are diffracted at specific angles, creating a pattern that relies upon the crystal's structure. The principle of XRD is encapsulated in Bragg's Law ( $n\lambda = 2d \sin\theta$ ) [183], which relates the wavelength of the X-rays to the spacing between crystal planes and the diffraction angle. By analyzing the diffraction patterns, the crystal's atomic arrangement can be determined. Many XRD analyses uses the  $\theta$ -2 $\theta$  configuration as shown in Fig. 2.9 [184]. Here, the sample remains stationary while the detector moves together with the X-ray source. Essentially, the detector angle (2 $\theta$ ) is always twice that of the incident X-ray beam angle ( $\theta$ ), hence the name  $\theta$ -2 $\theta$ . The simplicity and precision of the  $\theta$ -2 $\theta$  setup make it a standard in many XRD analyses.



Figure 2.9: Schematic of the XRD system showing  $(\theta - 2\theta)$  configuration. [184]

The XRD system at the COOC, UNCC (PANalytical X'Pert Pro/MRD) utilizes Cu K $\alpha_{avg}$  radiation at  $\lambda$ =1.5418A. (=1240/0.15418 = 8.04 KeV), created by directing accelerated beam of electrons from W filament to bombard Cu target. It uses the same  $\theta$ -2 $\theta$  configuration as described. It is versatile in its applications, particularly well-suited for thin films, including tasks like reciprocal space mapping and rocking curve analysis, phase analysis, as well as analysis of residual stress and texture.

#### 2.4.5 Atomic Force Microscopy (AFM)

AFM, belonging to the Scanning Probe Microscopes (SPMs) family, is used to analyze material surfaces from atomic to micron scales. It features a sharp, micron-long tip, often under 100Å wide, at the end of a 100 to 200µm cantilever. A detector measures the cantilever deflection resulting from the interaction between this tip and the sample surface. As the tip moves across the sample (or vice versa), these deflections are recorded and used to create a surface topography map. [185] The AFM system at UNCC features a Dimension 3100 (Digital Instruments, Veeco) with NanoScope IV Controller. Measurements are possible through Contact mode (uses an etched single crystal Si probe, TESP) or Tapping mode (Uses a Si<sub>3</sub>N<sub>4</sub> probe, DNP).

#### 2.4.6 Raman Spectroscopy

Raman spectroscopy, a vital tool in scientific research, primarily focuses on understanding the vibrational modes of molecules. This technique is centered on the Raman effect [186], which involves the inelastic scattering of monochromatic light when it interacts with molecular vibrations in a sample. Typically, a laser is used. As the light scatters, it experiences a shift in energy, corresponding to the molecule's vibrational energy levels in the specimen. Raman spectrum is obtained by gauging the scattered light's intensity and its wavelength shift from the incident light. Each mode is related to a particular molecular bond or group within the molecule, making the Raman spectrum effectively a molecular fingerprint. Vibrational modes are represented using four letters: A, B, E, T. A and B indicate singly degenerate vibrations, while E and T show doubly and triply degenerate vibrations, respectively. When radiation interacts with a lattice, it induces vibrations throughout the lattice. These vibrations can be longitudinal (L) or transversal (T) and range from low-energy (Acoustic) to high-energy (Optic) types. [187]

By analyzing the Raman spectrum, one can deduce information about bond lengths, bond angles, and other structural details at a molecular level. It is particularly useful at identifying different functional groups, symmetries, and even the orientation of molecules in a crystal lattice. Its non-destructive nature and minimal requirement for sample preparation further enhance its applicability across various fields like chemistry, materials science, and biotechnology.

In this research, Raman measurements were obtained by the confocal Raman microscope equipped with a 532 nm laser and a 1200 g/mm grating (Horiba LabRam HR800). A long-working-distance 100X microscope lens with NA = 0.9 was used to focus the beam on the specimen. The laser beam (532 nm) delivered to the stage w/o filter was ~20 mW, and ~120  $\mu$ W with a D2-filter. With the x100 objective (NA=0.9), the power density was ~2 x 10<sup>4</sup> W cm<sup>-2</sup>.

#### CHAPTER 3 : CVD GROWTH OF SILICON TELLURIDE AND SILICON

## 3.1 Introduction

Discovered two centuries ago [86, 88], silicon (Si) has been subjected to rigorous scientific scrutiny, making it one of the most extensively researched elements in modern history. We now have a comprehensive and precise understanding of its properties, and its applications are vast and continually expanding in this era dominated by silicon technology. Conversely, Si<sub>2</sub>Te<sub>3</sub>, introduced in the 1950s [26], has not garnered similar attention or seen widespread application. While information about this material is available, it isn't exhaustive. Many of Si<sub>2</sub>Te<sub>3</sub>'s properties and potential applications remain incompletely understood, with several possibly awaiting discovery in the scientific community.

## 3.1.1 Properties and Applications of Silicon

Si, constituting 27.2% by weight, is the second most prevalent element in the Earth's crust after O at 45.5%. [87] The term originates from the Latin words 'silex' or 'silicis', which translate to 'flint' or 'hard stone'. Si, is a semiconductor with an atomic number of 14, is a group 14 or IVA (C, Si, Ge, Sn, Pb) element with properties that are distinctively different from carbon and, conversely, from the heavier metals in the same group. The isolated Si atom in its neutral state has the electron configuration [Ne]  $3s^23p^2$ . Its melting point is at 1,414 °C (2,577 °F), and boiling point is at 3,265 °C (5,909 °F). Its density is 2.33 g/cc. Ionization energy 8.1517 eV. [188]

It has two main allotropes- crystalline (c-Si) and amorphous (a-Si). There is also porous silicon (p-Si) and nanocrystalline silicon (nc-Si). Single-crystalline and polycrystalline Si can again be regarded as distinct allotropes due to their significantly differing properties. Amorphous, or microcrystalline, Si is a black to brown powder. The structure of amorphous Si is flexible because some atoms aren't fully bonded, exhibiting a coordination number of 3.79-3.88, while crystalline

Si has a coordination number of 4.0. [189]. Polycrystalline silicon is grayish and metallic in appearance. Amorphous Si also exhibits significantly different electrical properties than crystalline Si, often owing to inherent hydrogen which passivates electronic defects. [190, 191] Porous silicon (p-Si), first reported by Uhlir [192], is a form with nanoscale pores in its microstructure. If they are made sufficiently small, as in the case of nanocrystalline silicon [191, 193], they display photoluminescence at room temperature.

Crystalline Si forms a diamond cubic structure [194] with a tetrahedral bond arrangement (Fig. 3.1). It has a lattice constant 5.43095 Å at 25°C, relating to a Si-Si nearest neighbor distance of 2.35Å and a covalent atomic radius of 1.18 Å. The diamond cubic structure of silicon features an FCC lattice with a two-atom basis at 0 0 0 and ¼ ¼ ¼, yielding an atomic packing factor of 0.34; which is just 46% of the packing factor of a close-packed structure, indicating its relatively open arrangement.



Figure 3.1: (Left) 2D projection of atom positions within the cubic unit cell of the diamond structure. (Right) Crystal structure of diamond. [194]

The electrical conductivity of Si can be altered by doping and through temperature variations. [195, 196] For intrinsic Si, the conductivity solely relies thermally produced carriers, and as the temperature rises, its resistivity decreases, which is characteristic behavior for a semiconductor. Pure Si features an indirect, indirect bandgap that is relatively narrow, at 1.12 eV, with the Fermi level positioned at the midpoint between the valence band (VB) and the conduction band (CB). The typical intrinsic resistivity of silicon ranges from  $10^{-1}$ - $10^5 \Omega$ -cm which effectively renders it an insulator at room temperature; however, as the range suggests, the actual resistivity can vary greatly depending on its purity. Doping Si with even a small amount of impurity atoms can make it n-type [197] or p-type [198] and can lower its resistivity by several orders of magnitude. It is possible to tune the electrical conductivity by changing the dopant concentration to match the specific needs of the desired device. Carrier mobility in Si is also greatly impacted by temperature and doping. Amorphous Si is found to have high resistivity on the order of  $10^{15} \Omega$ -cm, making it a great insulator. [190] Room temperature thermal conductivity of crystalline Si is about 150 Wm<sup>-</sup> <sup>1</sup>K<sup>-1</sup>, about a 100 times more than that of amorphous Si [199].

All allotropes of Si are well investigated using Raman scattering measurements. Monocrystalline silicon exhibits a shift in the first-order one phonon Raman peak at  $520.2\pm0.5$  cm<sup>-1</sup> which is symmetric and has a full width at half maximum (FWHM) of approx.  $4\pm2$  cm<sup>-1</sup> at room temperature [200-202] The Raman spectrum for amorphous silicon (a-Si) typically peaks around 480 cm<sup>-1</sup> and is characteristically faint in intensity and broad. A combined scenario where monocrystalline and amorphous or microcrystalline Si would both be present is presented in Fig. 3.2 [203]. Similar behavior is observed in black Si where the amorphous Si surface is doped with Te [204], where it is also shown that annealing at 600°C in N<sub>2</sub> for 30 mins can alter the amorphous Si into crystalline which is evident in Fig. 3.3.



Figure 3.2: a) Raman spectrum of a) monocrystalline silicon, b) amorphous-Si:H, and c) a and b combined and scaled (solid line). [203]



Figure 3.3: Raman spectra of the the processed silicon sample without annealing (red dash dot) and with annealing (blue solid) and unprocessed silicon (black dot). Scaled to show clearly in the insert. [204]

In micro- or polycrystalline Si (pc-Si), when the grain size is sufficiently reduced, there is a notable decrease in the Raman shift, an increase in the peak width and asymmetry of the peak, characterized by an elongated tail on the lower frequency side. [205] Raman on ~20  $\mu$ m avg. size Si microparticles exhibited the peak around 515 cm<sup>-1</sup> [206] (Fig. 3.4). In polycrystalline Si, other peak shifts are also identified, both at lower, and at higher end [193] (Fig. 3.5). While sharp peak



Figure 3.4: Raman spectrum of the Si particles. [206]



Figure 3.5: Raman spectrum of the luminescent nc-Si film deposited by PECVD. [193]

at 517 cm<sup>-1</sup> provides proof for high crystallinity, the lower-end peak shifts located at around 150 cm<sup>-1</sup> and 300 cm<sup>-1</sup> are due to the transverse acoustic phonons of crystalline Si [193, 206]. In crystalline Si, two overtones of transverse optical phonon manifested as a broadband peak between 900-1000 cm<sup>-1</sup> [193, 206]. Any band in between would be due to a mixture of optical and transverse acoustic phonons.

Raman on nanocrystalline Si (nc-Si) thin films reveals the principal peak (18 cm<sup>-1</sup> FWHM) at 517 cm<sup>-1</sup>, which is 3-4 cm<sup>-1</sup> red-shifted from the typical location for monocrystalline Si at 521 cm<sup>-1</sup> [193, 202, 207-209].

Mechanical stress can cause red/blue-shift from theoretical value. Redshift may possibly be attributable to the tensile strain induced by the substrate [210]. Blue-shift of Raman peak from 520 cm<sup>-1</sup> may originate from the presence of the compressive stresses in the structure. [211, 212] Thermal annealing caused by ion implantation can also induce such shifts. In such case the phonon structure of the damaged layer bears similarity to that of typical amorphous Si. [213]

Fig. 3.6 shows an obtained XRD from the Si particles powder in the  $2\theta$  range of  $10-80^{\circ}$  (CuKa radiation of 1.5418 Å), confirming the crystalline structure of the silicon particles as indicated the



Figure 3.6: XRD data for cubic Si [206]

presence of various sharp peaks. The spectrum displays diffraction peaks at  $2\theta$  values of  $28^{\circ}$ ,  $47^{\circ}$ ,  $56^{\circ}$ ,  $69^{\circ}$ , and  $76^{\circ}$ , which correspond to the (111), (220), (311), (400), and (331) planes respectively, for cubic Si structure (JCPDS card No. 27-1402). The peak corresponding to the (111) reflection exhibited the highest intensity. [206]

Hydrogenated amorphous silicon (a-Si:H) is widely used in the electronics industry for producing thin-film solar cells, IR sensors, and TFTs, thanks to its very high absorption coefficient. [106] Si microparticles are used as supercapacitors [206] Porous silicon (p-Si) with direct band gap [214] shows strong visible photoluminescence at room temperature under low-power laser excitation [215] nanocrystalline silicon (nc-Si) holds promise as a material for optoelectronics without oxygen involvement, silicon-based memory devices, and solar energy applications. [191]

Te doped Si is a potential candidate material for use in high-temperature extrinsic Si infrared detector, and high-response photodiode. Their distinctive absorption properties are advantageous for photovoltaic applications. [216-221].

Amorphous silicon nanowires (a-SiNWs) may hold potential for use in high-capacity portable rechargeable batteries [68]
## 3.1.2 Properties and Applications of Silicon Telluride

Si<sub>2</sub>Te<sub>3</sub> is a bright red, Si-based 2D layered chalcogenide with a MoS<sub>2</sub>-like trigonal structure in the  $p\bar{3}1c$  space group [151, 154, 222, 223], It was previously thought to resemble the CdI<sub>2</sub> structure amid formula debates [26, 129]. Unlike CdI<sub>2</sub>'s octahedral cations, MoS<sub>2</sub> features trigonal prismatic cations. Weak van der Waals forces hold together the stacks of atomic layers in 2D layered materials. [136, 149, 224]. The crystal structure of Si<sub>2</sub>Te<sub>3</sub> consists of Si–Si dimers occupying two-thirds of the octahedral vacancy sites formed inside HCP Te sublattices as shown in Fig. 3.7 [142, 143]. The dimers alignment leads to unique, chemically tunable [137] optical and electronic properties like broad near-infrared photo-luminescence (PL). Si<sub>2</sub>Te<sub>3</sub> has a direct optical bandgap near 2 eV which explains most of the spectral absorption and at least one forbidden indirect gap at lower energy [27, 35, 130, 142, 143, 148, 163].



Figure 3.7: Si<sub>2</sub>Te<sub>3</sub> crystal structure (a) Perspective top view, (b) Perspective side view, (c) Top view, and (d) side view of the Si<sub>2</sub>Te<sub>3</sub> crystal. (e–g) Various orientations of dimers. Te atoms are depicted in gray, while Si atoms are represented in blue. [142, 143]

XRD analysis has been used to confirm the crystal structure. The Rietveld refinement of the XRD spectra (Fig. 3.8 [36]) determined the hcp lattice constants for Si<sub>2</sub>Te<sub>3</sub> to be a =  $7.419 \pm 0.01$  Å and c =  $13.513 \pm 0.01$  Å, with peaks corresponding to JCPDF 00-022-1323. [36]



Figure 3.8: XRD spectrum of Si<sub>2</sub>Te<sub>3</sub> nanoplates. [36]

Fig. 3.9 shows Raman on  $Si_2Te_3$  nanoplates from Keuleyan [36]. Vertical nanoplates (a) show a strong out of plane  $A_{1g}$  mode at 137 cm<sup>-1</sup> and a weaker in-plane  $E_g$  mode at 474 cm<sup>-1</sup>. Additionally, there are several  $E_g$  peaks present near 326 cm<sup>-1</sup>, which align with the intense absorption line previously noted in IR studies [33]. The broad peak around 3200 cm<sup>-1</sup> is from the photoluminescence of the  $Si_2Te_3$  nanoplates at 641 nm (1.9 eV), indicative of its direct band gap. For the flat plates (b), a doublet at 123.9 cm<sup>-1</sup> is detected, corresponding to a transverse optical (TO) mode identified in IR measurements, and another peak at 143 cm<sup>-1</sup> which is possibly attributable to the  $A_{1g}$  mode, along with several  $E_g$  modes at 275.6 cm<sup>-1</sup> and 484.4 cm<sup>-1</sup>.



Figure 3.9: Raman spectrum of Si<sub>2</sub>Te<sub>3</sub> nanoplates. [36]

Recently, Hathaway [155] investigated the degradation of Si<sub>2</sub>Te<sub>3</sub> nanoplates and noted that the degraded Si<sub>2</sub>Te<sub>3</sub> exhibits Raman spectroscopy results very similar to those of pure Te, as illustrated in Fig. 3.10. (Left) Freshly prepared and unaltered Si<sub>2</sub>Te<sub>3</sub> has only one prominent Raman peak at 144 cm<sup>-1</sup>. The Raman spectra typically documented in earlier sources [36, 137, 139, 150, 151, 154] feature two primary peaks, similar to Fig. 3.10, suggesting that these samples were of degraded Si<sub>2</sub>Te<sub>3</sub> containing Te as the degradation byproduct [31]. This elucidates that the presumed A<sub>1g</sub> mode in Si<sub>2</sub>Te<sub>3</sub> nanoplates corresponds to Te's A<sub>1</sub> mode. (Right) Raman spectra from a Si<sub>2</sub>Te<sub>3</sub> nanoplate at 0.5 mW laser power show A<sub>1</sub> and E<sub>2</sub> modes of Te and A<sub>1g</sub> mode of Si<sub>2</sub>Te<sub>3</sub>. Initially, a small ~120 cm<sup>-1</sup> peak and a sharper ~144 cm<sup>-1</sup> peak with a shoulder are seen. With increased laser exposure, the ~120 cm<sup>-1</sup> peak grows, and the ~140 cm<sup>-1</sup> shoulder becomes dominant after 15 seconds, indicating two distinct peaks, separated by 3–4 cm<sup>-1</sup>, rather than one. The proximity of these two ~140±3 cm<sup>-1</sup> peaks likely caused previous oversight.



Figure 3.10: (Left) Raman spectra of unaltered Si<sub>2</sub>Te<sub>3</sub>, degraded Si<sub>2</sub>Te<sub>3</sub>, Te, and TeO<sub>2</sub>. (Right) Raman spectra of Si<sub>2</sub>Te<sub>3</sub> nanoplate following consecutive in situ heating with laser at a power of 0.5 mW. [155]

As mentioned previously, the main challenge associated with Si<sub>2</sub>Te<sub>3</sub> crystals is that they quickly hydrolyze upon exposure to air from vacuum, although eventually developing a protective Te film, inhibiting further decomposition. This surface reaction is detailed in [31]

$$Si_2Te_3(s) + 4H_2O(g) \rightarrow 2SiO_2(s) + 2H_2Te(g) \uparrow + Te(s) + 2H_2(g) \uparrow$$

The existence of Te and SiO<sub>2</sub> on the surface was confirmed through chemical analysis, and  $H_2Te$  is easily identifiable by its distinct smell [28]. The Te layer typically forms even at very low partial pressure of  $H_2O$  which makes handling and storing a challenging task. Restoration of the crystal surface by removing Te coating may ideally require some form of surface treatment, e.g. vacuum sublimation, to be applied before use [34]. Fig. 3.11 illustrates how fast it decomposes in contact with air. [156].





Apart from the highly hygroscopic nature, Si<sub>2</sub>Te<sub>3</sub> exhibits problematic doping characteristics. It is inherently p-type regardless of doping. The resistivity of stoichiometrically grown undoped Si<sub>2</sub>Te<sub>3</sub> prepared by quench-anneal method is typically found to be  $\sim 10^2$ - $10^3 \Omega$ -cm at room temperature. Even a shift of 1 at% to either side from its stoichiometric ratio was found to potentially increase the resistivity by up to  $10^2$ - $10^3$  times. Other dopants such as As, Fe, Cd, Cu, Ga, and Mn typically increase the resistivity by up to  $10^5$ - $10^6$  times at concentrations of  $\sim 10^{20}$  atoms/cm<sup>3</sup>, with exception such as Sb, which lowers the resistivity to the order of 1  $\Omega$ -cm. [28, 31] Among other unique properties, Si<sub>2</sub>Te<sub>3</sub> possesses inherently defective crystal structure, leading to other interesting properties like very low thermal conductivity (1-5 mW/°C·cm) and Hall mobility (< 1 cm<sup>2</sup>/V·s). [31]

Although  $Si_2Te_3$  has been primarily utilized for research, despite the challenges, it is gaining interest due to its compatibility with established Si technology and its unique structural variations, including its advantages as a 2-D layered material. [157, 163] Si<sub>2</sub>Te<sub>3</sub> nanoplates has been demonstrated as a chemically tunable substrate with a comprehensive range of optical properties, making it a promising candidate material for optoelectronic applications. [137, 154]. Exploration of Si<sub>2</sub>Te<sub>3</sub> single crystals in Field effect phototransistor (FET) and photodetector applications, interfaced with a rigid silicon substrate, has revealed remarkably enhanced performance compared to those recorded for other 2D chalcogenide materials such as  $Bi_2Te_3$  and  $Sb_2Te_3$ . [153]  $Si_2Te_3$  is a p-type semiconductor and shows a broad spectral response (405–1064 nm). With just 13.5 nm thickness, it reaches a photoresponsivity of 65 AW<sup>-1</sup> and detectivity of  $2.81 \times 10^{12}$  Jones at 405 nm, outperforming typical broadband photodetectors. These findings showcase Si<sub>2</sub>Te<sub>3</sub>'s potential benchmarks for the next generation of p-n junction circuits and photodetection technologies. [143] Group-IV n-type tellurides such as PbTe, GeTe or SnTe and other 2D chalcogenides, especially  $Bi_2Te_3$  has been widely used as cutting-edge thermoelectric materials in power generation. Doped Si<sub>2</sub>Te<sub>3</sub>, with its calculated ultra-low thermal conductivity of 2 Wm<sup>-1</sup>K<sup>-1</sup> and groundbreaking ZT of 1.86 at 1000 K, holds promise as a leading material for future thermoelectric power generation. [225, 226]

## 3.1.3 CVD Growth of 3D Silicon and 2D Silicon Telluride Structures

3D Silicon and 2D Silicon Telluride structures were grown in a custom-made CVD chamber. The CVD growth is for Si film, particles, microwires, or nanowires, not Si wafers. The details of the growth process and parameters are provided in the previous section. Several series of experiments were carried out to obtain structures that can be broadly categorized into three major groups as follows:

- 1. Non-catalyst growth
- 2. Catalyst-assisted growth
- 3. Control experiments for mechanism study

## 3.2 Experimental

## 3.2.1 Non-Catalyst Growth

In a typical non-catalyst growth experiment, approx. 250 mg of Te powder was placed 3 inches upstream from the central location, which is 4 inches from either side (Fig. 3.12). Approx. 60 mg of Si powder was then placed at the center of the furnace. This was followed by the growth substrate, placed 3 inches downstream from the center, coated with SiO<sub>2</sub> layer over Si. The chamber was then pumped down to a vacuum pressure of approximate 10 mTorr. 20 SCCM of UHP Ar was introduced into the chamber as a carrier gas for vapor precursor transport. After stabilizing the Ar flow using the mass flow meter, 5 SCCM of UHP H<sub>2</sub> was introduced as a



Non-catalyst growth



reductive gas to remove and prevent possible oxidation of the powders or substrates from residual oxygen inside the system. Once both the Ar and  $H_2$  gas flows had stabilized, the furnace was heated to 850°C in a ramp time of 15 minutes. At the start of the ramping time, the initial system pressure was set to 10 Torr. As the temperature increased, Te began to evaporate first due to its low melting point, causing the pressure to start rising. Once the pressure reached the desired value (e.g., 100 Torr for typical growth), during the heating cycle, it was maintained at this level using the automatic pressure control system. As the temperature reached 850°C, it briefly overshot to 861°C but then stabilized back to 850°C within two minutes. This temperature was maintained for the total growth duration of 60 minutes, followed by a gradual cooldown of the system to room temperature over several hours.

In another non-catalyst growth experiment, a bare Si (111) substrate was placed approximately one inch next to the Si powder, as illustrated in the schematic in Fig. 3.13. This was to ascertain if, for the catalyst-assisted growth, any reaction that might happen—whether it would be due to the catalyst's role, from the extra Si (111) substrate, or a combination effect of both.



Figure 3.13: Schematic of typical growth without catalyst (no coating on the Si (111) substrate).

#### 3.2.2 Catalyst-Assisted Growth

In a typical growth experiment using catalysts, a metal-coated Si (111) substrate, usually with Cu, was added as shown in the Fig. 3.14. Approximately 250 mg of Te powder was placed 3 inches upstream from the central location, which is equidistant, 4 inches, from either side. Then, approximately 60 mg of Si powder was placed at the center of the furnace. This arrangement was followed by placing a Cu- or Au-coated Si (111) substrate 1 inch downstream from the center. Finally, the main growth substrate, coated with either a  $SiO_2$  layer over Si, was positioned 3 inches downstream from the center. For the remainder of the growth process, the same steps as those used in the non-catalyst growth were followed.



Figure 3.14: Schematic of typical growth with catalyst.

## 3.2.3 Control Experiments for Mechanism Study

To understand the mechanism of growth enhancement, control experiments were performed (Fig. 3.15a). In the first set of experiments Te was used as source material and the morphology of additional Si (111) substrates, bare and coated with a layer of Au (10 nm) or Cu (~5 nm) were examined. Approximately 250 mg of Te powder was placed 3 inches upstream from the central location and Cu- or Au-coated Si (111) substrate placed 1 inch downstream from the center. For the rest of the growth process, the procedures followed were identical to those employed in the growth without a catalyst. The other set of annealing experiments were performed without the supply of source material for further clarity. (Fig. 3.15b)



Figure 3.15: Schematic of typical control (annealing) experiments. (a) with source (Te) and (b) without source powder.

## 3.3 Results and Discussion

The as-grown samples were meticulously characterized using OM, SEM, and EDS. Prior to discussing them, it is crucial to emphasize some characteristic growth features, as they offer invaluable insights and further substantiate the reactions occurring during the process.

After a typical non-catalyst growth cycle, a deposit was observed in and around the growth zone, as shown in the Fig. 16. On the high-temperature (HT) side, approximately 780–750°C, a brownish deposit was noted, followed by a bright red deposit in the region of approximately 750–600°C. Eventually, a mirror-like silvery deposit was observed in the lower temperature zone, around 600–400°C. The Te powder had completely evaporated, while the Si powder appeared to have undergone almost no change (Fig. 3.17b).

In terms of the appearance of deposition and reaction, the results from the catalyst assisted growths were similar to non-catalyst growth, but with some subtle changes in appearance. Similar depositions were observed in and around the growth zone, as shown in the figure. On the HT side, approximately 780–750°C, a brownish deposit was seen, followed by a bright red deposit in the region of approximately 750–600°C. In the lower temperature zone, around 600–400°C, a mirror-



Figure 3.16: Non-catalyst growth. CVD chamber (a) before and (b) after growth. Source and substrate (c) before and (d) after growth.

like silvery deposit was noted. However, the deposition appeared to be thicker compared to the non-catalyst growth. The Te powder had completely evaporated, but this time there was a noticeable grayish or light-colored layer on top of the Si powder, indicating clear signs of a chemical reaction (Fig. 3.17c). The darker color of the boats is due to their prolonged use.



Figure 3.17: Appearance of the Si powder: (a) before, and (b) & (c) after growth for non-catalyst growth, and catalyst-assisted growth respectively.

For the annealing processes with Te, only a silvery deposit of Te was formed on the tube. All of source Te were evaporated in the process.

### 3.3.1 Non-Catalyst Growth of Silicon Telluride

For non-catalyst growth, with or without the added Si (111) substrate, three distinct zones can be identified from the OM and SEM images as shown in Fig. 3.18. The formation of the zone is believed to be primarily due to the substrate temperature, while vapor transport only affects the density and size of the deposition. [227] Zone I is the high temperature end where deposition occurs between 780-700 °C and is characterized by large (10 microns or larger), thick (~2-5 $\mu$ m), overlapping plates. Zone II occurs between 700-500 °C, and larger flat islands to smaller particles, from high to low temperature respectively, are formed. They are usually visible to the naked eye. Occasionally, smaller and vertical flakes are seen to grow out of them in various places. All these



Figure 3.18: Zones in non-catalyst growth. (a) photo showing the panoramic view of the growth, (b) Zone I showing thick  $Si_2Te_3$  plates, (c) Zone II showing large  $Si_2Te_3$  islands, (d) Zone III showing smaller, thin  $Si_2Te_3$  flakes with serrated edges, and (e) EDS of the plates in zone I.

plates, or island shapes are observed to be of hexagonal shaped and appears as if they are made of thin sheets being progressively stacked on top. In Zone III, much smaller flakes are seen to grow, inclined at an angle with the substrate, and have less defined edges. The composition of these structures is confirmed to be Si<sub>2</sub>Te<sub>3</sub> using EDS.

3.3.2 Catalyst Assisted Co-Growth of 3D Silicon and 2D Silicon Telluride

From the optical micrograph and SEM images (Fig. 3.19), three distinct zones, very similar to those observed in non-catalyst growth, are evident on the growth substrate, as shown in the figure. However, there are some novel features.

Zone I begin at the high-temperature end, typically extending from  $780^{\circ}$ C to  $650^{\circ}$ C. The description showcases large, horizontal plates with a unique characteristic: the accumulation of cubic particles on their surfaces, preferentially along the edges. It's challenging to ascertain the exact dimensions of these overlapping plates, but they are generally observed to exceed 50 µm in



Figure 3.19: Zones in catalyst-assisted growth. (a) photo showing the panoramic view of the growth, (b) Zone I showing  $Si_2Te_3$  plates and Si particles, (c) Zone II showing islands and smaller particles of  $Si_2Te_3$ , and (d) Zone III showing inclined and vertical thin plates of  $Si_2Te_3$ .

size. The Si particles typically range from 3~7 µm, with a common average diameter of about 5

 $\mu$ m. A closer look (Fig. 3.19b, inset) at these particles reveal possibility of them being polycrystalline, as evident from the different facets at different crystallographic orientations.

In zone II, the formation of both sizable islands and smaller particles is evident. These structures are thought to originate from the evaporation and subsequent solidification of Te droplets, which are initially deposited on the substrate. These Te pools can expand to sizes between  $100-300 \ \mu\text{m}$ . Si<sub>2</sub>Te<sub>3</sub> materializes as substantial, flat, singular crystals spanning  $1-150 \ \mu\text{m}$ . The larger islands possess a layer of hexagonally shaped flat plates and towering formations, potentially developed during the initial growth phase. When examined at a lower magnification, these islands resemble dried-out large liquid droplets, leaving some residue behind. The smaller particles often display protrusion of thin vertical plates, less than 5 micrometers in size, indicative of the secondary growth stage. Finally, in zone III, the emergence of small (less than 5 micrometers) and slanted or vertical thin plates is observed. These plates progressively diminish in size as the temperature decreases and typically are hemi-hexagonal shaped.

EDS analysis, as presented in Fig. 3.20, was used to shed light on the compositional details of the observed structures. The quantitative results of the EDS analysis are calculated with the assumption of a homogenous composition distribution. The calculations are presented in Table 3.

Si Si Overall SiO<sub>2</sub> Layer Si<sub>2</sub>Te<sub>3</sub> Plates Locations Substrate Particles Si:O<sup>1</sup> Si:Te:O Si:Te Si Si Zone I: Particles 96.72:3.28:0 0:0 0  $2:19:3.28^2$ 94.53 26.02:46.92 = 0 Zone I: Plates 35.04:46.92:18.04 9.02:18.04 unknown 1:1.80 34.38:47.56 =Zone II: Plates 40.40:47.56:12.04 6.02:12.04 0 unknown 1:1.38 Zone III: 43.69:6.96:49.35 24.68:49.35 19.01:6.96 = 1:0.370 unknown Nanoplates

Table 3: Calculations of Si, Te and O from EDS data

<sup>&</sup>lt;sup>1</sup> Estimated using O signal with Si:O = 1:2 for SiO<sub>2</sub>

<sup>&</sup>lt;sup>2</sup> Estimated using Te signal with Si:Te = 1:1.5 for Si<sub>2</sub>Te<sub>3</sub>



Figure 3.20: Zones in non-catalyst growth. (e) Photo showing the panoramic view of the growth, (f) Zone I, (g) Zone II, (h) Zone III, and (i) EDS of the plates in zone I.

However, our samples here have a non-uniform composition distribution as different layers were deposited at different heights, resulting in the results with small deviations from the actual values.

Zone I-Particles: No O signal was detected, indicating the deposition on the substrate was thick enough that no signals were from the  $SiO_2$  layer and the underneath Si substrate. If we assume the 2D plates are  $Si_2Te_3$  deposition, the extra Si signal of 94.53 at% shows the 3D particles on the top is Si particles.

Zone I-Plates: Using the O signal, the Si signal from the  $SiO_2$  layer can be estimated. After deducting the signals from the  $SiO_2$  layer, the Si:Te for the plates is estimated to be 1:1.80, which

is slightly different from the 1:1.5 for  $Si_2Te_3$ , indicating the plate composition is very close to  $Si_2Te_3$ . The slightly lower Si signal also confirmed that there was no Si signal from the Si substrate underneath the SiO<sub>2</sub> layer.

Zone II-Plates: Similarly, after deducting the signals from the  $SiO_2$  layer, the Si:Te for the plates is estimated to be 1:1.38. The slightly higher Si signal is attributed to the additional Si signal from the Si substrate for this detected location.

Zone III-Nanoplates: Both the O and Si signals are extraordinarily high, showing strong signals from the substrate due to the thin thickness of the nanoplates. After deducting the signals from the  $SiO_2$  layer, the Si:Te for the nanoplate is estimated to be 1:0.37, with unignorable Si signal from the underneath Si substrate.

In the case of the larger islands, the Si:Te ratio was found to be around 1:1.4, slightly deviating from the anticipated 1:1.5 ratio. This discrepancy was primarily due to the influence of the silicon substrate. Thin Si<sub>2</sub>Te<sub>3</sub> structures show a disproportionately high Si signal, with a Si:Te ratio nearing 1:0.37, largely affected by the background substrate material. These compositional characteristics of the plates are consistent with existing literature reports.

Backscattered electron (BSE) imaging, as seen in Fig. 3.21 were obtained to quickly check composition using contrast variations corresponding to the differing compositions within the sample. It was observed that structures with a higher proportion of tellurium (Te), a heavier element, appeared brighter in the BSE images. This correlation suggests that BSE imaging, being a rapid and easily switchable mode from standard SEM, can be an effective and efficient method for preliminary identification and analysis of structures. Given a basic understanding of the constituent elements, BSE imaging can serve as a useful tool in both laboratory and industrial

settings for assessing bulk sample growths, offering a time-saving alternative to the more timeintensive EDS analysis.

Fig. 3.21 shows the XRD data<sup>3,4</sup> from zone I. The strong Si (004) peak is from the Si (001) substrate. The very small Si (111) peak (inset shows an enlarged view) is from the Si particles in Zone I. The peak is weak due to the small amount of the Si particles and their narrow growth area with Zone I.



Figure 3.21: XRD analysis from zone I.

Besides SEM, EDS and XRD, Raman measurements were also taken to get information about the structures. The measurements from zone I is presented in Fig. 3.22. It is to note that at 1% power Si<sub>2</sub>Te<sub>3</sub> plates got damaged from the heat, but at 0.1% and 0.01% power there was no visible damage to the sample after the measurements. However, the peak intensities were higher at 1% power but overall the peaks showed no shift due to change in power. Si particles did not get damaged at 1% power. [The laser beam (532 nm) delivered to the stage without filter was ~20 mW

<sup>&</sup>lt;sup>3</sup> Si reference: ICDD 00-005-0565

<sup>&</sup>lt;sup>4</sup> Si2Te3 reference: ICDD 00-022-1323



Figure 3.22: Raman measurements (graph on right side) of  $Si_2Te_3$  plates and Si particles in zone I. The OM photo on the left shows the location of the Raman measurement, inset shows similar region in SEM. (Courtesy: Dr. Young Zhang group)

and with a D2-filter it would be ~120  $\mu$ W. With the x100 objective (NA=0.9), the power density would be ~2 x 10<sup>4</sup> W cm<sup>-2</sup>].

The true Si<sub>2</sub>Te<sub>3</sub> peaks at lowest laser power should be used to identify the plate phase. At low laser power, pristine Si<sub>2</sub>Te<sub>3</sub> plates showed peak at ~144.8 cm<sup>-1</sup>. At higher power, it degraded to form Te and showed additional strong peaks at around ~124 cm<sup>-1</sup> and ~143 cm<sup>-1</sup> [156]. However, weaker peaks at ~326 cm<sup>-1</sup> and ~474 cm<sup>-1</sup> [139] are not seen which would be assigned to multiple  $E_g$  modes in the 2D Si<sub>2</sub>Te<sub>3</sub> nanoplates. Also, no peak showing definitive presence of TeO<sub>2</sub> are observed. [155] The Si particles are found to show peak position at 519.2 cm<sup>-1</sup> which is close to well documented values of ~520 cm<sup>-1</sup> for crystalline Si. [209]

Raman measurements with corresponding SEM image of the Si<sub>2</sub>Te<sub>3</sub> plates and substrate in zone II is shown in Fig. 3.23 below. The peaks appeared at ~125 cm<sup>-1</sup> and ~144 cm<sup>-1</sup> for Te and 2D Si<sub>2</sub>Te<sub>3</sub> plates (similar to zone I), and the top of the towering structures showed a little red shift (~7 cm<sup>-1</sup>) in both peak positions (~117 cm<sup>-1</sup> and 137 cm<sup>-1</sup>) from the Si<sub>2</sub>Te<sub>3</sub> plates to the Si<sub>2</sub>Te<sub>3</sub> towers (higher bond length, smaller wave number) suggesting possible small tensile strain in the towers. The ~144 cm<sup>-1</sup> peak was stronger at the bottom plate, suggesting probable lower degree of



Figure 3.23: (a) OM and (b) SEM images of the  $Si_2Te_3$  plates and towering structures on the large particles in zone II, and (c) corresponding Raman spectra (Courtesy: Dr. Yong Zhang group)

conversion from Si<sub>2</sub>Te<sub>3</sub> to Te at the bottom plate, and higher percentage of Te at the tower top.

[209]

Raman measurements with corresponding SEM image of the Si<sub>2</sub>Te<sub>3</sub> plates and substrate in zone III is shown in Fig. 3.24 below. The peak position for Si<sub>2</sub>Te<sub>3</sub> plates appeared at ~125 cm<sup>-1</sup> and ~143 cm<sup>-1</sup>, when compared to the plates in zone I and zone II, suggests that there are no strains in the Si<sub>2</sub>Te<sub>3</sub> plates. The substrate Si peak appeared at 521 cm<sup>-1</sup>, about the same location as the Si particles in zone I (519 cm<sup>-1</sup>). The small difference (~2 cm<sup>-1</sup>) could be due to structural changes induced by defect in the Si particles (e.g. by oxygen) rendering small tensile stress to the structure.



Figure 3.24: (a) OM and (b) SEM images of the Si<sub>2</sub>Te<sub>3</sub> plates and substrate in Zone III, and (c) corresponding Raman spectra (Courtesy: Dr. Young Zhang group)

## 3.3.3 Growth Mechanism Analysis

To understand the growth mechanism, several series of experiments were carried out. The foremost ones are classified as annealing experiments as mentioned previously (refer to Fig 3.15).

In the first set of such experiments, Te was used as source material and the morphology of additional Si (111) substrates, bare and coated with a layer of Au (10 nm) or Cu (~5 nm) were examined. In the second set of annealing experiments were performed without the supply of source material for further clarity.

Without catalyst coating i.e. for bare Si (111), substrate surface was found to be primarily smooth with fewer etching pits and small amount of particle growth (Fig. 3.25a). EDS analysis confirmed these are Si particles. When the growth chamber was vacuumed immediately after growth, these particles appeared in much lesser extent. This was to prove the hypothesis that they resulted from the limited reaction of the substrate with the Te and Si vapor, which were predominantly deposited from the vapor species during the later/cooling stage of the growth.

For Cu/Si (111) and Au/Si (111) substrates, etching pits and nanowires were found for both cases in the first few experiments. Etching pits were more prevalent on the Cu/Si (111) with a small number of short nanowires (Fig. 3.25b). However, it was later confirmed that the etching pits on the Au/Si (111) resulted from Cu contamination in the coating. Likewise, the small number of short nanowires on Cu/Si (111) samples could possibly be attributed to Au contamination in the coating. Long nanowires are dominant on Au/Si (111) covering the etching pits on the substrate surface (Fig. 3.26c). The nanowires are expected to be SiO<sub>x</sub> nanowires formed by the VLS growth on Si (111) as reported by our group's previous study. [62]



Figure 3.25: After-growth morphology on (a) bare Si (111), (b) Cu/Si (111), and (c) Au/Si (111).

Annealing experiments showed small circular droplets in the case of Au since Au do not react with Si at the growth temperature and pressure (Fig. 3.26b). Triangular and hexagonal shapes in the case of Cu were observed because Cu can react with Si somewhat more readily than other metals [164] and may only penetrate the top of the substrate surface. (Fig. 3.26a). Cu is also much cheaper compared to Au.



Figure 3.26: After-annealing morphology of (a) triangular island from Cu contamination and (b) Au particles on Si without Cu contamination.

The reaction mechanism steps when Cu is used as catalyst are depicted in Fig. 3.27. First, when the coated substrate is heated at sufficiently high temperature, Cu forms triangular or semitriangular shaped Cu-Si alloy islands with the Si (111) substrate. The incoming Te adsorbs into this island and forms Cu-Si-Te ternary alloy islands forming eutectic particles. At the growth temperature, as time passes, more Si comes from the substrate into the eutectic particles forming shallow etching pits. Simultaneously, due to thermodynamic equilibrium, Si-Te species escape from these particles at a higher rate than incoming molecules and the shallow etching pit gets larger and deeper. Thus dense, large, and deep etching pits are created. The enhancement of Cu as catalyst can be explained by the eutectic formation. It was reported [36] that Te<sub>2</sub> vapor does not react strongly with Si at low heating temperatures (<750 °C) to form Si<sub>2</sub>Te<sub>3</sub> species which was verified using Cu and Si mixture for growth in the Future Work (Section 5.2). However, Cu, Te, and Si can form eutectics between each other at much lower temperatures as shown by the phase diagrams in (Fig. 3.28). [28, 228, 229]



Figure 3.27: The reaction mechanism steps (a) Cu forming Cu-Si alloy islands and particles with Si (111) substrate, (b) The incoming Te and Cu-Si alloy islands forming eutectic particles, (c) formation of shallow etching pits, and (d) formation of dense, large, and deep etching pits.



Figure 3.28: Phase diagrams for Si-Cu [227], Si-Te [28], and Cu-Te [228] systems.

When Te-Cu-Si ternary eutectic forms on the Si (111) substrate, the Te content in the eutectic is reduced due to evaporation and Si-based vapor species are subsequently released from the eutectic back into the CVD chamber in the downstream. The etching pits and local growth of nanowires on Cu/Si (111) substrates indicate that the Si (111) substrates serve as additional Si source with the presence of Cu and Au catalysts. Thus, the presence of Cu or Au on the Si (111) substrates can promote the Te-Si reactions by the formation of Te-Cu-Si and Te-Au-Si ternary eutectics producing more  $Si_2Te_3$  and Si species for the deposition on the downstream  $SiO_2$ -Si substrate. This is proposed to be the VLV mechanism as shown in Fig. 3.29.

The Si-based vapor species deposit onto the growth substrate in two ways.



Figure 3.29: Schematic drawing of stages in proposed VLV process.

First, Si-Te deposits in the stoichiometric ratio of 2:3 to form the hexagonal shaped  $Si_2Te_3$  plates through VS mechanism (Fig. 3.30). The growth of crystals via this mechanism is influenced by surface energy, yet it primarily operates as a kinetic growth process, not a thermal equilibrium growth process. [39] In contrast, a thermal equilibrium growth process is entirely governed by



Figure 3.30: VS growth of 2D Si<sub>2</sub>Te<sub>3</sub> crystals.

surface energy and results in crystals with equilibrium shapes that typically lack high aspect ratios. However, in the kinetic VS growth process, the growth of crystals is directed by the anisotropic structure and varying growth rates across different crystal faces. This process leads to the formation of crystals with high aspect ratios—shapes that are elongated rather than uniform.

Second, exclusively in the catalyst assisted growth, as the Si-Te vapor rich in Si cools down, Si is deposited as cubic Si particles which is also a VS mechanism. Since they lay on top of the  $Si_2Te_3$  plates, it is evident that they form at the later stage of growth. The schematic of this process is shown in Fig. 3.31.



Figure 3.31: Si vapor production through VLV process and VS co-growth of 3D Si and 2D  $Si_2Te_3$  crystals.

For further understanding, it is useful to describe the vapor pressure. Fig. 3.32 shows the vapor pressure of Te, Cu, Au, and Si at different temperatures. As it is evident from Fig. 3.32, a summary of which is presented in Table 4, Cu, Au, and Si have almost negligible vapor pressures ( $<10^{-5}$  Torr for Cu,  $<10^{-7}$  Torr for Au and  $<10^{-8}$  Torr for Si) even at the maximum heating temperature which is lower than 850 °C, and thus can be ignored. Te has a very high vapor pressure (>1 Torr when heated above 550 °C). At the 100 Torr total growth pressure, however, the partial pressure of Te vapor is limited by its saturation pressure at Te source heating temperature. Only a supersaturation allowed for the downstream location for deposition.



Figure 3.32: Vapor pressure chart of element materials with Te, Cu, Au, and Si data highlighted. [courtesy VEECO, edited]

Temperature (°C)	597°C	723°C	844°C	838°C	808°C	677°C	390°C
Те	~3	~45	~110	~105	~25	~11	~0.011
Si	< 10 <sup>-8</sup>						
Au	< 10 <sup>-8</sup>	< 10 <sup>-8</sup>	< 10 <sup>-7</sup>	< 10 <sup>-7</sup>	< 10 <sup>-7</sup>	< 10 <sup>-8</sup>	< 10 <sup>-8</sup>
Cu	< 10 <sup>-8</sup>	< 10 <sup>-8</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-5</sup>	< 10 <sup>-8</sup>	< 10 <sup>-8</sup>

Table 4: Vapor pressure at different temperatures in Torr [VEECO]

Fig. 3.33 illustrates the growth variation at different growth pressures. At 100 Torr and 50 Torr pressure, on the high temperature end of the growth substrate (at 7" location) large plates of Si<sub>2</sub>Te<sub>3</sub> are formed along with Si particles in zone I. However, at 10 Torr pressure, smaller plates of Si<sub>2</sub>Te<sub>3</sub> are seen to form in zone I, and no Si particles are observed. And many of the Si<sub>2</sub>Te<sub>3</sub> plates are found to be dissociated due to Te evaporation at low pressure. Therefore, it can be concluded that for effective reaction of Te with Si and its stability, higher pressure would be necessary. In zone II, a lot more of big particles are seen to form at 100 Torr than at 50 Torr. Which also suggests that higher pressure helps forming Si<sub>2</sub>Te<sub>3</sub> and once formed it is more stable at a higher pressure. In

zone III, smaller  $Si_2Te_3$  are seen to form at all pressures. But at lower pressure they are found to become more flat or horizontal than vertical.



Figure 3.33: SEM and BSE images of (left) Zone I, (center) Zone II, and (right) Zone III from growths at different pressures of (top) 100, (middle) 50, and (bottom) 10 Torr

# 3.3.4 Residual Effects of Tellurium

In some of the annealing experiments, where no Te was used, little amount of etching would still be seen. This was likely due to residual Te in the CVD system from typical experiments. It was, therefore, important to clean the system from time to time.

#### CHAPTER 4 : TWO-STAGE AND LIQUID PHASE EPITAXIAL GROWTH

### 4.1 Introduction

Several experiments were carried out to better understand the stages of growth. The growth morphologies at different growth times provided valuable insights into the steps.

## 4.2 Experimental

For time evolution experiment, the experimental part is the same as described before in Chapter 3. The only difference is the growth time which were varied between 0 min to 60 mins. For Liquid phase epitaxial growth, a layer of Te was deposited on the growth substrate (SiO<sub>2</sub>-Si) first, followed by the regular process of catalyst-assisted growth in a separate experiment.

## 4.3. Results and Discussion

Time evolution study was carried out for both non-catalyst growth and catalyst-assisted growth.

## 4.3.1 Time Evolution Study of Two-stage growth

For non-catalyst growths, macroscopically, similar depositions are observed for different growth times (0, 15 and 60 min) except for that longer growth time facilitates extended growth zones and increased amount of deposition as shown in figure. SEM images reveal detailed morphology changes as show in Fig. 4.1. At the high temperature end (left panel), the deposition changed from dense hemispheric particles to large flat crystals, and almost merged together with the increase of the growth time. More to the right nearing middle with colder temperature (middle panel), the deposition was particles with a significant bimodal size distribution. They also changed their shapes from being hemispheric to being flatter with the increase of growth time. Towards the low temperature end (right panel), small hemispherical particles changed to vertical or angular flakes. Element analysis using EDS confirmed the composition of the 0 min growth is dominantly

Te with small amount of  $Si_2Te_3$  at the surface. For the 60 min growth, the composition of the large crystals is mainly  $Si_2Te_3$ .



Figure 4.1: (Left panel) Photos of overview of depositions on SiO<sub>2</sub>-Si substrates with growth time of 0 min, 15 min, and 60 min. (Right panel) SEM images of depositions on SiO<sub>2</sub>-Si substrate grown with different growth times at (left) high temperature end (~1 mm from the left edge), middle (~10 mm from the left edge), and (right) low temperature end (~20 mm from the left edge).

Further investigation into growth during the heating cycle is shown in Fig. 4.2. Heating was stopped promptly when the system temperature reached 500 °C and 600 °C, and then cooled down to room temperature. It is to note that actual temperature at growth location is lower. In both cases, both zones I and II were seen to get identical depositions that look like tubular or rod shaped. At 500°C, the crystals appear to be hollower than at 600°C. EDS confirmed these crystals to be purely of Te. In these experiments, as the system was cooling down, growth of these Te crystals were thermodynamically favored. However, in heating cycles as in the regular experiments, these crystals would melt as the temperature went up and formed into liquid droplets before reacting with the incoming Si-Te species or evaporating as shown previously in Fig. 4.1.



Figure 4.2: (Left panel) Photos of overview of depositions on SiO<sub>2</sub>-Si substrates with ramping time of 9 min (500°C), 11 min (600°C). (Right panel) SEM images of depositions on SiO<sub>2</sub>-Si substrate grown with different growth temperatures at (left) high temperature end (~1 mm from the left edge), and (right) lower temperature end (~10 mm from the left edge).

Therefore, the study of the growth time effects indicates a two-stage growth during the deposition: Firstly, Te crystals form first at low heating temperature during ramping period which is uniform across the substrate with deposition density and size change gradually. The Te deposition subsequently melts with the further increase of substrate temperature forming Zone I and Zone II. With the high temperature at Zone I, previous deposition mostly melts and evaporates, and the growth is then dominated by the second stage deposition. While, at Zone II, the deposition melts and turns into large droplets, followed by dense deposition forming around the large droplets during the second stage. Secondly, as the system temperature reaches the growth temperature and as it is being held there, Te vapor in the chamber reacts with Si powders promoting the deposition of Si<sub>2</sub>Te<sub>3</sub> crystals and the conversion of Te droplets into Si<sub>2</sub>Te<sub>3</sub> crystals takes place. This continues as long as there is Te supply, and it was found that after 60 minutes, no Te was left in the boat. It was thus decided to use 60 min reaction length time for all future reactions so that maximum

growth of the Si<sub>2</sub>Te<sub>3</sub> plates can be achieved with limited source material. Si has high melting temperature ( $T_m = 1400^{\circ}C$ ) and does not transport without Te but can react with Te<sub>2</sub> vapor. Tellurium vaporizes at much lower temperature ( $T_m = 450^{\circ}C$ ) and forms Te<sub>2</sub> precursor and transports Si as SiTe after reacting with Si powder.

For catalyst-assisted growth (Fig. 4.3), the growth at 0 min was very similar to the non-catalyst growth, consisting mostly of Te deposits. The growth at 30 mins showed the second stage growth of  $Si_2Te_3$  plates had taken place. Between 35-40 mins growth time, Si crystal started to grow along the edges and on top of the  $Si_2Te_3$  plates in zone I through VS mechanism as explained previously in Section 3.3.3 with the help of the schematic shown in Fig. 3.31.



Figure 4.3: (Left panel) Photos of overview of depositions on SiO<sub>2</sub>-Si substrates with growth time of 0 min, 30 min and 40 min. (Right panel) SEM images of depositions on SiO<sub>2</sub>-Si substrate grown with different growth times at (left) high temperature end (~1 mm from the left edge), middle (~10 mm from the left edge) and (right) low temperature end (~20 mm from the left edge).

### 4.3.2 Liquid Phase Epitaxial Growth

During the first stage of growth, Te crystals deposited at the Zone II of the growth substrate which liquifies into droplets. As temperature was increased, some of these droplets stayed in place while others subsequently evaporated. The ones that stayed acted as seeds and facilitated the growth of  $Si_2Te_3$  via quick diffusion of SiTe species on the liquid Te surface forming a thin  $Si_2Te_3$  layer across the surface. The later  $Si_2Te_3$  growth is then a form of homogeneous growth on this  $Si_2Te_3$  layer, therefore the growth is the highly oriented as shown below in Fig. 4.4. As previously described in Section 3.3.3, this VS growth process is influenced by surface energy, often resulting in the formation of crystals in crystallographically favorable orientations, such as hexagonal shapes. It is characterized by the development of crystals with high aspect ratios—shapes that are elongated rather than uniform, resembling towering structures akin to a city skyline.



Figure 4.4: Examples of pseudo-epitaxially grown  $Si_2Te_3$  in non-catalyst growth. (a) Thin  $Si_2Te_3$  layers as round-shaped islands with later  $Si_2Te_3$  growth on them, (b) 30° side view of a single tower, and (c) and (d) show close-up views of the highly oriented growth, featuring straight and tapered towers, respectively.

## **CHAPTER 5 : SUMMARY AND FUTURE WORK**

#### 5.1 Summary

The primary objective in this thesis was to understand the vapor transportation and growth mechanisms of Si and Si<sub>2</sub>Te<sub>3</sub> crystals using CVD. The motivation included identifying or developing a growth model. In this study, co-growth mechanism of 3D Si crystals with 2D Si<sub>2</sub>Te<sub>3</sub> crystals in CVD growth using Te and Si powders as the source materials in the presence of a Cucoated Si substrate was explored. For typical growth, ~250 mg Te and ~60 mg Si powders were loaded upstream and the catalyst coated substrate followed by the growth substrate were placed downstream. A temperature gradient of about  $\sim 200 \,^{\circ}\text{C}$  existed across the growth substrate resulting in three distinct zones based upon growth morphology. In zone I towards the high temperature end, large, horizontal, and thicker plates of 2D Si<sub>2</sub>Te<sub>3</sub> and 3D Si particles were formed. In zone III towards the low temperature end, smaller, thin, and horizontal, vertical or inclined 2D Si<sub>2</sub>Te<sub>3</sub> flakes were formed. In between these two zones, larger to small island shaped 2D Si<sub>2</sub>Te<sub>3</sub> particles were formed with distinguished pseudo-epitaxial, towering growths. The 2D Si<sub>2</sub>Te<sub>3</sub> growth was explained by the conventional VS growth mechanism. The 3D Si growth was found to be promoted by the synergetic effects of Cu and Te. Cu as a stable catalyst were found to facilitate the reaction of Te vapor species with the Si substrate, forming ternary Te-Cu-Si eutectics. Due to the instability of Te, the Te-Cu-Si eutectic particles evaporated and released Si vapor as the precursor for the Si crystal growth. A new VLV precursor formation mechanism was proposed: providing a new approach for the material growth at lower growth temperature and lower cost, making it more compatible for device fabrications.

5.2 Preliminary Results of Enhanced Growth using Mixed Copper/Silicon Source

It was shown that Cu can enhance growth of  $Si_2Te_3$  where Te-Si precursors were passed over a Cu coated Si (111) substrate. Instead of using Cu coated Si (111) as catalyst and Te and Si as separate source materials, Cu powder was used where Si and Cu, and Si, Cu, and Te powders were mixed together in different compositions at different temperatures. A schematic of this is shown below in Fig. 5.1.



Figure 5.1: Schematic of the growth setup with catalyst powder mixed with source.

These early experiments showed some promising results. Three distinct zones are identified as shown in Fig. 5.2 which is similar to the previously mentioned report for catalyst assisted growth. However, in Zone I, the Si particles appear to have smaller facets and somewhat round shaped.



Figure 5.2: Zones in mixed-catalyst growth. (a) photo showing the panoramic view of the growth, (b) Zone I showing thick  $Si_2Te_3$  plates with dense Si particles, (c) Zone II showing  $Si_2Te_3$  islands and (d) Zone III showing smaller, thin  $Si_2Te_3$  flakes with smooth edges.

EDS analysis (Fig. 5.3) showed about 0.08 atom% Cu, which doped the Si particles and possibly attributed to the roundness. The thick Si<sub>2</sub>Te<sub>3</sub> plates extend much further into zone II, showing significant improvement in Si<sub>2</sub>Te<sub>3</sub> growth. In Zone III, similar thin, vertical and inclined hemi-hexagonal flakes of Si<sub>2</sub>Te<sub>3</sub> are found. The growth mechanism is the same as previously explained in catalyst-assisted growth in Section 3.2.2. Si<sub>2</sub>Te<sub>3</sub> plates grow via VS mechanism, while the VLV process from the Te-Si-Cu ternary alloy occurring at the source-catalyst mixture promotes the growth of the Si particles. A schematic is shown in Fig. 5.4 below. SEM images of the Cu-Si







Figure 5.3: SEM (top panel) and corresponding EDS (bottom panel) on Si particles for Cu-Si mixed source.



Figure 5.4: Schematic of the growth mechanism with catalyst powder mixed with source.

powder after growth show etching pits, a clear proof of reactions taking place (Fig. 5.5). Growth at different temperature showed that a minimum of  $750^{\circ}$ C is required for Si<sub>2</sub>Te<sub>3</sub> to favorably grow.



Figure 5.5: SEM images showing etching pits on the Si particles in the Si-Cu powder after growth.

## 5.3 Future Work

The thesis presented a comprehensive study on the growth process of 2D Si<sub>2</sub>Te<sub>3</sub> plates and 3D Si particles, laying a solid foundation for future research in this area. Building on this, several exciting avenues can be explored in future work.

Explore different substrates: Silicon wafers are available in various industry-standard orientations such as (100), (110), and (111), each tailored for specific semiconductor applications.

The (100)-oriented wafers feature rows of surface atoms that encourage the growth of oxides, leading to flat, hydrophobic surfaces suitable for crafting tiny features on sophisticated transistors and integrated circuits. The less common (110) orientation provides an asymmetrical surface structure that is advantageous for specialized devices, including niche MEMS and heterojunction bipolar transistors. The (111) orientation, historically significant for early transistor technology, supports very thin layering and precise dopant profiles, beneficial for high mobility charge carriers in certain analog ICs. Overall, while (100) wafers are predominantly used in advanced logic and memory chips, the (110) and (111) orientations offer unique attributes valuable for specialized applications. [230-232] In this study, Si (111) wafers were used as the catalyst coated source material. However, wafers with other orientations can be employed and they are expected to produce similar results as the catalyst coated Si substrates are used as a Si source for the reaction. For the growth substrate, Si wafers with different orientations, and substrates other than SiO<sub>2</sub>/Si can also be explored for epitaxial growth with lattice matching purposes.

Electrical Property Characterization: A detailed investigation into the electrical properties of both 2D Si<sub>2</sub>Te<sub>3</sub> plates and 3D Si particles is crucial. This can include measurements of conductivity, mobility, and carrier concentration. Techniques such as Hall effect measurement, four-point probe testing, and conductive atomic force microscopy can be employed to gain a deeper understanding of the material's electrical behavior.

Device Fabrication and Testing: The potential of Si<sub>2</sub>Te<sub>3</sub> and Si in device applications can be vast. Future work can focus on fabricating various types of devices such as transistors, sensors, and photovoltaic cells using these materials. The performance of these devices in terms of efficiency, durability, and scalability should be thoroughly assessed.

Surface and Interface Studies: Understanding the surface and interface properties of  $Si_2Te_3$  and Si is critical for device applications. Studies can be conducted to analyze how surface treatments and interface engineering affect the electrical and mechanical properties of these materials.

Theoretical Modeling and Simulation: Alongside experimental work, theoretical modeling and simulations can be performed to predict the behavior of these materials under different conditions. This can help in optimizing the material properties for specific applications.

Exploration of Heterostructures: Creating heterostructures by combining  $Si_2Te_3$  plates with other 2D materials such as graphene or integrating 3D Si particles with different matrices can open up new functionalities and applications. Investigating the synergistic effects in such heterostructures can be a fruitful area of research.

Thermal Property Analysis: Besides electrical properties, understanding the thermal properties of Si<sub>2</sub>Te<sub>3</sub> and Si is important, especially for high-power and high-frequency device applications. Studies can be conducted to measure thermal conductivity and analyze heat dissipation in these materials.

Environmental and Stability Testing: One of the main challenges for making Si<sub>2</sub>Te<sub>3</sub> device will be its stability. It is already well-known that it decomposes readily in air, making it imperative for us to find ways to prevent this. Assessing the stability of Si<sub>2</sub>Te<sub>3</sub> and Si under other environmental conditions (e.g. temperature variations, and exposure to different gases) is essential for practical applications. Long-term stability tests can provide insights into the reliability and lifespan of devices made from these materials.

Scalability and Commercialization Potential: Lastly, research should be directed towards the scalability of the production process of Si<sub>2</sub>Te<sub>3</sub> plates and Si particles. Assessing the commercial
viability and identifying potential industrial applications will be key to transitioning from laboratory research to practical, real-world applications.

Each of these areas not only extends the research conducted in the thesis but also contributes significantly to the field of materials science and nanotechnology, potentially leading to groundbreaking applications in electronics, energy, and other sectors.

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