Hybrid Physical-Chemical Vapor Deposition of Bi₂Se₃ Films

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Abstract: Bi₂Se₃ thin films were grown on c-plane sapphire substrates by hybrid physical chemical vapor deposition (HPCVD) using trimethyl bismuth (TMBi) and Se pellets. A Se-rich environment is created by evaporating Se pellets in the vicinity of the substrate, which is used to suppress the formation of Se vacancies. The effects of pre-cracking temperature and substrate/Se temperature on the growth rate, structural and electrical properties of the Bi₂Se₃ films were investigated. C-axis oriented films were obtained which show a reduction in the carrier concentration as pre-cracking temperature was increased from 290°C ($1.6 \times 10^{19} \text{ cm}^{-3}$) to 350°C ($8.4 \times 10^{18} \text{ cm}^{-3}$). An additional reduction in carrier concentration ($7.28 \times 10^{18} \text{ cm}^{-3}$) was observed on increasing the substrate temperature from 200 to 260°C.

Keywords: A1. Layered materials; A3. Hybrid physical-chemical vapor deposition processes; B1. Bismuth Selenide; B2. Topological Insulator

1. Introduction

Bi₂Se₃ is a promising topological insulator (TI) material due to its nearly-ideal band structure[1] and relatively high band gap energy (0.3eV) [2]. Further advances in the study of electrical transport in TI materials require the ability to form highly-oriented Bi₂Se₃ films directly on insulating substrates. The crystal structure and thermal stability of Bi₂Se₃ provides both advantages and challenges for epitaxial growth. The quintuple layered structure of Bi₂Se₃ [3] enables van der Waals epitaxy on lattice mismatched substrates. Thermal stability is also an issue for film deposition. Bi₂Se₃ has a melting temperature of 706°C and requires an overpressure of Se, when heated, to avoid the loss of Se and the formation of native Se vacancies (Se_{Se}) which act as double donors ($\text{Se}_{\text{Se}} \Leftrightarrow \text{V}_{\text{Se}} + \text{Se}(\text{g}) + 2\text{e}^-$)[4]. As a result, low growth temperatures (<300°C) and high Se/Bi ratios are typically advantageous for reducing the bulk electron concentration in the films. The bulk electron concentration acts as a parallel conduction path making it difficult to isolate the behavior of the topological surface states in transport measurements. Several methods have been pursued to circumvent this problem including the addition of compensating impurities such as Ca[5], Pb[6] and Sb[7] and the use of gated electrical

test structures which are used to deplete carriers from the bulk of the film[8]. However, there is significant interest in the development of methods to reduce the n-type conductivity in Bi_2Se_3 films without any additional manipulation.

We previously reported the growth of Bi_2Se_3 films by hybrid physical-chemical vapor deposition (HPCVD) using trimethylbismuth (TMBi) and Se pellets [9]. HPCVD combines thermal decomposition of a chemical precursor in conjunction with evaporation of an elemental source in close proximity to the growth substrate. This is a promising technique for the growth of Bi_2Se_3 because a higher Se/Bi (VI/V) ratio reduces the Se vacancy concentration, which in turn lowers the carrier concentration. The Se pellets are placed on the same heated susceptor as the substrate to ensure a high local partial pressure. This limits the substrate thermal exposure to temperatures near the melting point of Se (220°C) to prevent rapid evaporation of Se during growth. The low substrate temperature causes inefficient decomposition of the TMBi source. As a result, an additional resistance heater was placed upstream in the reactor to pre-crack the TMBi. In this manuscript, the effect of varying the TMBi pre-cracking temperature and substrate/Se temperature on the Bi_2Se_3 growth has been further explored. The pre-cracking of TMBi and vapor phase concentration of Se controls the growth rate and morphology. The lowest carrier concentration is achieved when both these parameters are optimized in tandem.

2. Experimental details

Sapphire (0001) wafers (Cryscore Optoelectronic Limited) were used as substrates for film growth. The substrates were cleaned by ultrasonication in acetone and isopropanol for 15 min followed by a de-ionized (DI) water dip and dried in a N_2 stream.

A schematic of the cold-wall HPCVD reactor chamber is shown in Figure 1. The susceptor was heated inductively to control the substrate and Se temperature. A second resistive heater was placed upstream of the susceptor to pre-crack the TMBi. The pre-cracking temperature was varied from $290 - 540^\circ\text{C}$ while substrate/Se was maintained at 220°C . At the pre-cracking temperature of 350°C , the substrate/Se temperature was varied from $160-280^\circ\text{C}$. The duration of the deposition was maintained such that all the films grown were 20-30 nm thick.

The TMBi source was held at -10°C and a pressure of 760 Torr in a stainless steel bubbler and H_2 carrier gas with a flow rate of 35 sccm was used which resulted in a TMBi flow rate of 0.245 sccm. Five pellets of Se, or 0.25g were placed in the ring around the sapphire (0001) substrate. Additional H_2 carrier gas was added to maintain a total flow rate of 100 sccm through the reactor which was held at a pressure of 100 Torr.

Glancing angle x-ray diffraction (Rigaku DMAX Rapid II) was used to determine the phases present. The crystal quality and orientation was determined using a four-circle x-ray diffractometer (Philips MRD). The surface morphology of the films was investigated by scanning electron microscopy (Phillips XL-20 and Zeiss LEO 1530). The thickness of the thin film samples was usually determined using a stylus surface profilometer (Tencor P-10). Atomic force microscopy (Digital Instruments Dimension 3100) was used to analyze the film surface and measure surface roughness. Large misaligned crystals were excluded from the roughness calculations in order to more accurately measure the underlying film roughness. Room temperature Hall-effect measurements were carried out using a custom-made system and indium contacts to determine the electrical properties of the Bi_2Se_3 films.

3. Results and Discussion

3.1. Effect of TMBi pre-cracking temperature

In the two-heater arrangement, the extent of pre-cracking of the TMBi source is dependent on the temperature of the resistance heater which, in turn, is expected to alter the growth rate and properties of the Bi_2Se_3 films. The effect of pre-cracking was ascertained by varying the top heater temperature from 290 – 540°C while the substrate/Se were maintained at 220°C. The surface of Bi_2Se_3 is made up mostly of triangular pyramidal structures. Increasing the top-heater temperature reduces the size and increases the density of the pyramids, as can be seen in Figure 2(a-b), when the temperature is raised from 290°C to 500°C. This causes a reduction in the RMS roughness of the films (blue dots, Figure 2(c)). This reduction in the size of the pyramids is attributed to the difference in growth rate (red dots, Figure 2(c)). At lower pre-cracking temperature, the film grows more slowly from fewer nucleation sites. These initial islands extend farther before they encounter each other and start to spiral due to pinning [10].

The x-ray diffraction data across the whole range of top heater temperatures studied showed strongly c-axis oriented films as shown in the representative theta-2theta scan in Figure 3(a) for films grown at 500°C. The phi scan of the off-axis (015) peak, shown in Figure 3(b), indicates that the film is well-oriented rotationally within the plane of the substrate. The inset in Figure 3(a) shows the rocking curve omega scans. The full-width half maxima (FWHM) of the (006) peak remains constant ($\sim 0.046^\circ$) throughout the temperature range studied. However, the shape of the rocking curve peak does change slightly over the temperature range studied. While the peaks for films grown at 350°C and 500°C are symmetrical, the peak for a film grown at 290°C is decidedly asymmetrical. This asymmetry may be attributed to a varying supply of Se over time. The growth time for 20-30 nm thick films at 290°C is approximately 11.5 mins which might cause Se depletion during the growth. As the Se supply depletes during growth, a slight change in the d-spacing might result, causing the asymmetry.

The most relevant effect of the pre-cracking temperature is on the electrical properties of Bi_2Se_3 . Figure 4 shows the room temperature Hall mobility (blue dot) and electron concentration (red triangle) of the films. From 320-540°C, there is a clear trend of higher electron concentration and lower mobility, with the carrier concentration increasing from $n=9.16 \times 10^{18} \text{ cm}^{-3}$ at 320°C to $n=1.47 \times 10^{19} \text{ cm}^{-3}$ at 540°C and mobility decreasing from $\mu=715 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $=552 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ over the same range.

The increase in electron concentration can be attributed to the higher top heater temperatures promoting decomposition of TMBi and a decreased VI/V ratio, thus increasing the Se vacancy concentration. The increased carrier concentration leads to greater ionized impurity scattering, and hence lower mobility, as seen in Figure 4. However, at 290°C, there is a sudden shift in this trend, with the carrier concentration shooting up to $1.67 \times 10^{19} \text{ cm}^{-3}$ and mobility decreasing to $509 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. This may be due to the relatively higher VI/V ratio eventually leading to Se_{Bi} antisite defects, which are formed in a Se rich ambient and act as electron donors [11].

3.2. Substrate temperature variation

The next study was to vary the bottom heater temperature from 160°C to 280°C while keeping the top heater constant at 350°C, which corresponds to the lowest electron concentration from the previous set of experiments. Growths at 160°C and 180°C yielded no deposition on the substrate. This is likely because the Se vapor pressure was insufficient to act as a supply for notable film growth. Significant growth did not begin until 200°C. The growth rate then increases with temperature over the range from 200 – 280°C. Figure 5 shows SEM images of samples grown at 200°C, 220°C, 260°C and 280°C. The insets in Figure 5(a-c) show the morphology at higher magnification. The sample grown at 200°C has a granular structure with small grains covering the surface. The samples grown at 220-260°C show similar large triangular pyramids with misaligned platelets on the surface. The out-of plane platelet density increases as the temperature increases from 220 - 280°C. The inset in Figure 5(d) shows the continuous film under the platelets at 280°C. This increase could be due to either a higher growth rate at higher temperatures or the higher substrate temperature allowing growth to partially overcome the weak van der Waals bonding, leading to more out-of plane growth.

For samples grown at 220°C and above, the x-ray data conforms to that described above for the top heater study. This means, as shown in Figure 6, that the (006) rocking curves had a very small FWHM (0.0511° at 260°C) and the phi scan of the (015) peak showed 6-fold symmetry. The sample grown at 200°C, however, shows a much broader and weaker rocking curve peak. It also does not exhibit the 6-fold symmetry of the (015) peak like the other films, which indicates that it is not single crystalline. At the other end of the substrate/Se heater temperature range studied, the film

grown at 280°C showed poor structural quality compared to the other samples. The film is clearly polycrystalline. This is also evident in an SEM image of the surface seen in Figure 5(d).

The bottom heater temperature also had a significant impact on the room temperature electrical properties of the films. As can be seen in Figure 7, the carrier concentration (red) decreases with increasing substrate/Se temperature while mobility (blue) increases over the same range. The electron concentration decreases significantly from $3.73 \times 10^{19} \text{ cm}^{-3}$ at 200°C to $7.28 \times 10^{18} \text{ cm}^{-3}$ at 260°C. This translates to a sheet carrier density of $1.45 \times 10^{13} \text{ cm}^{-2}$. This is comparable to the lowest sheet carrier densities obtained by MBE in the recent years on sapphire. A reduction by another order of magnitude is achieved by introducing a In_2Se_3 interlayer [12]. This large change between 200°C and 220°C is likely related to the increase in crystallinity. This change could also be due to melting of Se which causes an increase in its vapor pressure. This overall trend is likely due to an increase in the VI/V ratio, and thus a decrease in Se vacancies due to higher Se vapor pressure at higher bottom heater temperatures. The drop in mobility above 240°C is likely due to the increased platelet density at 260°C, where the misaligned platelets act as scattering centers. Electrical measurements were not carried out on the sample grown at 280°C due to the very large platelet density.

4. Conclusions:

The two-heater configuration used in HPCVD allows efficient decomposition of TMBi while maintaining the substrate at a lower temperature. Using this configuration, c-axis oriented Bi_2Se_3 films were synthesized at substrate temperatures of 220-260°C. The Se/Bi ratio, which controls the electron concentration, could be controlled by regulating the pre-cracking and substrate/Se temperature. Lowest electron concentration of $7.28 \times 10^{18} \text{ cm}^{-3}$ was obtained at the substrate/Se temperature of 260°C and top heater temperature of 350°C.

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Figure 1. Schematic of HPCVD growth system with two heater setup.

Figure 2. (a)AFM of samples grown with a pre-cracking temperature of 290°C, (b)AFM of samples grown with a pre-cracking temperature of 500°C and (c) Growth rate and RMS roughness variation with temperature.

Figure 3. Typical XRD data for two-heater HPCVD-grown film, (a) theta-2theta (inset is the rocking omega curve) and (b) 360 phi scan of (015) peaks. Inset shows the rocking curve of the (006) peak for samples grown at 290°C (FWHM = 0.0475°, red), 350°C (FWHM = 0.0441°, blue), and 500°C (FWHM = 0.0463°, green).

Figure 0. Room temperature Hall-effect mobility and electron concentration versus pre-cracking temperature.

Figure 5. SEM images for samples grown at pre-cracking temperature of 350°C and substrate/Se temperature of (a) 200°C, (b) 220°C, (c) 260°C and (d) 280°C. Higher magnification images of the films are included as insets. Note that the inset in (d) is a cross-section image of the sample.

Figure 6. X-ray rocking curves of the (006) peak for samples grown at 200°C (FWHM = 0.1022°, red), 220°C (FWHM = 0.0422°, blue), 260°C (FWHM = 0.0511°, green), and 280°C (FWHM = 0.0347°, purple).

Figure 7. Room temperature Hall-effect mobility and electron concentration versus substrate/Se temperature.