Application of a Graphene Buffer Layer For The Growth of High Quality SnS films on GaAs(100) Substrate

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***Abstract* — Tin mono-sulfide (SnS) thin films have been grown by molecular beam epitaxy (MBE) on two different substrates, GaAs (100) and soda lime glass at 400^{o}C. High resolution X-ray Diffraction (HXRD) and Scanning Electron Microscopy (SEM) are used to characterize the structural properties of the as grown SnS films. By introducing a graphene buffer layer between the SnS thin film and the substrate, the XRD rocking curve's full width at half maximum (FWHM) of the SnS film grown on GaAs (100) and soda lime glass decrease from 2.92^o to 0.37^o and from 6.58^o to 2.04^o respectively, indicating a significant improvement of SnS thin films.**

***Index Terms* —scanning electron microscopy, X-ray diffraction, molecular beam epitaxy, graphene, Gallium arsenide.**

I. INTRODUCTION

Layered materials, such as graphene and many transition metal chalcogenides, have demonstrated attractive electronic and optical properties for the application of high performance nano-electronic and optoelectronic devices. [1-3]. Tin mono-sulfide (SnS) is a layered material and is commonly referred to as a Van der Waals Epitaxy (VdWE). It has an orthorhombic structure with a = 3.987Å, b = 11.200Å, and c = 4.334Å.[4] It is a semiconductor with a direct bandgap of ~1.0eV and an indirect band gap of ~1.3eV.[5] The unit cell of SnS crystal consists of two unit layers, which are stacked perpendicularly along the b axis. The layers are binded together by weak van der Waals force while atoms within a unit layer are bonded by strong covalent bonds. This material shows attractive properties which may find important photovoltaic applications such as: non-toxic and cheap; appropriate band gap; high absorption coefficient ($\alpha > 10^4$cm^{-1}) near the band edge. [4, 5] The as-deposited SnS films exhibited p-type conductivity [6] and may potentially be used as the photovoltaic absorber layer. Although the SnS material exhibits desirable photovoltaic properties, very few studies about this material focused on the growth of high quality films.

Several methods have been used for the deposition of SnS films, including chemical bath deposition[7], electrochemical deposition[8], vacuum thermal evaporation[9], and plasma chemical vapor deposition[10] … etc. Low light conversion efficiency could be expected for the solar cells using such poor quality SnS films. Boonsalee.[8] reported the growth of SnS films on single crystal Au substrate by electrochemical deposition technique. The average FWHM of SnS XRD rocking curve peak is around 3.16°. It will be quite difficult to fabricate high performance photovoltaic cells using such poor quality films. Therefore, further improvements in the film quality are needed for the development of high efficient solar cells.

Several research groups have reported SnS-related solar cells. Although the theoretical limit in the conversion efficiency of SnS-based solar cell is ~25%,[11] the results of previous works were much lower than the theoretical prediction (no more than 1.3%)[12]. One of the most important reasons is the inability to grow high quality SnS films on substrates with large lattice mismatch. In this paper we demonstrate a novel growth technique that leads to drastic relaxation of requirement for lattice match between the film and the substrate by inserting a graphene buffer layer between the SnS film and the substrate. Both SnS and graphene are layered materials, therefore, high quality graphene might be a good substrate for the SnS layer.

II. EXPERIMENTAL DETAILS

In our work, the SnS thin films were grown in an MBE system, in which 99.99% purity SnS compound was used as the evaporation source. The deposition rate of the SnS films was controlled at ~1μm per hour by adjusting the SnS k-cell temperature and the typical thickness of the as-deposited SnS films is 1μm.

From the point of view of lattice match, GaAs (100) substrate might be a good candidate for the growth of high quality SnS film. The lattice mismatch between SnS and GaAs (100) is −0.26% and 8.42% with respect to the "a" and "c" axis of SnS. Thus both GaAs (100) and soda lime glass were investigated as substrate and the growth temperature was kept at 400°C to suppress the formation of other tin sulfide phases such as SnS_2, Sn_2S_3, and Sn_3S_4 … etc. In order to improve the crystallinity of the SnS films, a study on the growth of SnS on layered material on graphene buffer layer, was performed. This is accomplished by layer transfer of high quality, large area bi-layer graphene buffer layers onto the GaAs(100) and soda lime glass substrates which were deposited on Cu foil by Chemical Vapor Deposition (CVD).

III. Results and Analysis

According to the XRD results, when the substrate temperatures are kept at 400°C, the crystallinity of the SnS demonstrates a strong dependency on the substrates. Fig. 1 shows two theta-omega XRD spectra of SnS films grown on four different substrates: GaAs (100), soda lime glass, graphene/GaAs (100) and graphene/glass as represented by solid lines of different colors. It is observed that SnS films deposited on GaAs exhibit stronger SnS diffraction peaks than that grown on glass and exhibit only two SnS diffraction peaks corresponding to (040) and (080) plane at 2θ= 31.89° and 66.55° respectively, indicating preferential [010] orientation of the film. The results are the same with SnS films grown on graphene buffer layer. As shown in Fig.1, SnS deposited on graphene/GaAs (100) show much stronger diffraction peaks than that deposited on graphene/glass substrate and only two SnS diffraction peaks corresponding to (040) and (080) plane are observed.

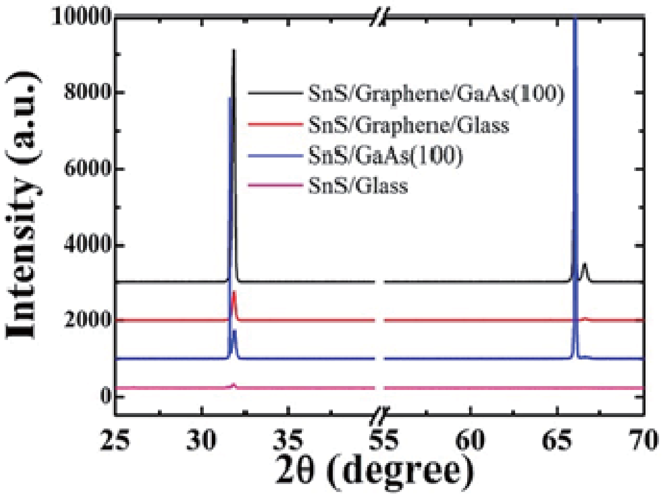

Fig. 1. Two theta-omega XRD spectra of SnS grown on four kinds of substrates: GaAs (100), soda lime glass, graphene/GaAs (100) and grapheme/glass represented in different colours.

For SnS films grown on graphene/glass, the intensity of SnS diffraction peaks are comparable with those directly grown on GaAs(100). The strong reflection peaks of SnS on graphene/GaAs indicate bi-layer graphene covered GaAs(100) is an appropriate substrate for the growth of high quality SnS thin film.

Base on the HXRD and SEM results, a significant improvement on SnS film quality and crystallinity is observed for films deposited on graphene/GaAs(100). Figure 2 shows the rocking curves of the (040) reflection of SnS deposited at 400°C on different substrates. The FWHMs of X-ray rocking curves of (040) reflection of SnS on GaAs, soda lime glass, graphene/GaAs, and graphene/glass are 2.92°, ~ 6.58°, 0.37°, and 2.04° respectively. It can be concluded that significant improvement in the crystallinity is achieved by introducing a double layer graphene between SnS and substrate. To the best of our knowledge, 0.37° is the best rocking curve FWHM value ever reported in the literature. It is worth noting that graphene covered glass substrates are not as good as graphene covered GaAs(100) substrate for the growth of high quality SnS films. This result could be attributed to the difference of the surface roughness between soda lime glass and GaAs(100).

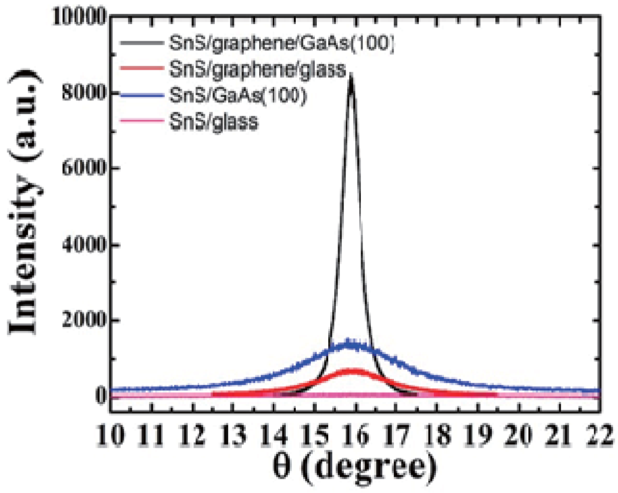

Fig. 2. X-ray rocking curves of SnS(040) on GaAs, glass, graphene/GaAs, and graphene/glass with FWHMs of 2.96°, ~ 6.58°, 0.37°, and 2.10° respectively.

SEM pictures of SnS deposited on different substrates, soda lime glass, GaAs(100), and graphene/GaAs(100), with growth temperature at 400°C are shown in Figure 3. It is observed that flake like structures exist on the surface of the SnS films deposited on glass, while SnS films grown on GaAs(100) exhibit smooth surface, the grain size of those films are very small. For SnS films deposited on graphene/GaAs(100), both smooth surface and larger grains are observed.

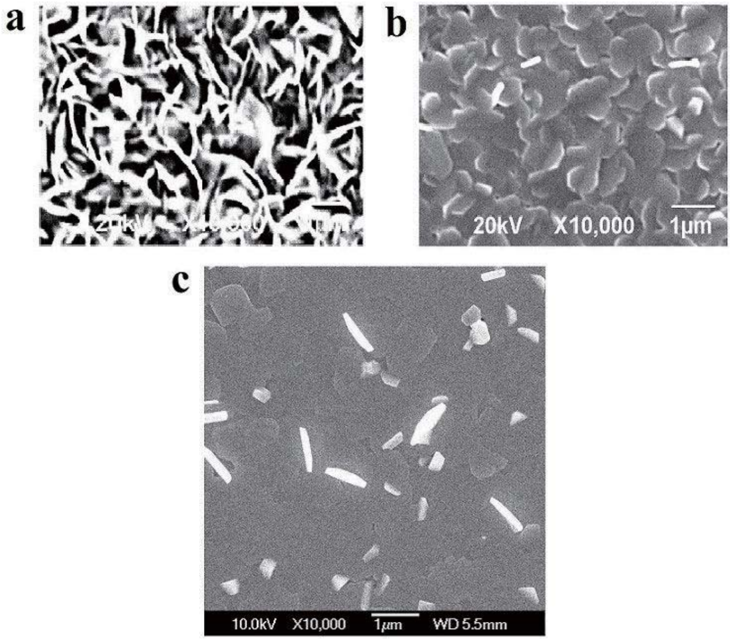

Fig. 3. SEM top view of SnS deposited at 400^{o}C on a)glass, b)GaAs(100), and c)graphene/GaAs(100)

IV. Conclusions

In conclusion, the effect of graphene buffer layer on the growth of high quality SnS films by MBE was investigated. Significant improvement on both the grain size and rocking curve FWHM of the SnS films were observed for films grown on graphene/GaAs(100) at typical substrate temperature (400^{o}C). This indicates significant improvement in the crystallinity of the as-grown films. The XRD results are consistent with the experimental data on the SEM pictures of the films in which SnS film deposited on graphene/GaAs (100) substrates demonstrate significant improvement in the morphology of the films. To further improve SnS film quality, the deposition and transfer process of graphene buffer layer should be optimized.

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