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The evolution of bond structure in $Ge_{33}As_{12}Se_{55}$ films upon thermal annealing

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ABSTRACT

The evolution of bond structure of laser deposited $Ge_{33}As_{12}Se_{55}$ films under various processing conditions has been investigated by X-ray photoelectron spectroscopy. It was found that a large number of Se-rich structures in the as-grown film may coalesce with As and Ge after annealing at high temperatures. In addition, both Ge and As 3d spectra show the presence of oxides. The oxygen distribution exponentially decays along the normal direction of the films regardless of different processing conditions. The critical thickness of the oxidized layer was extracted for the film annealed at various pressures and temperatures.

1. Introduction

Chalcogenide $Ge_{33}As_{12}Se_{55}$ glasses are promising candidates for fabricating non-linear optical waveguide devices due to their large third order optical non-linearity [1,2]. Films of chalcogenide glass deposited by physical vapor deposition onto an oxidized silicon wafer are generally used to fabricate waveguide structures. A significant issue for chalcogenide devices is that the films, unlike the bulk glass, have unstable physical properties which usually degrade the device performance and reliability. The instabilities generally arise because the films are prepared under non-equilibrium conditions and this leads to different bond configurations from the bulk material [3,4]. When thermal/optical annealing methods were applied to accelerate the relaxation of the film structure close to the bulk, oxidation could be simultaneously induced. However, there is no systematic investigation on the evolution of the bond configuration upon thermal annealing and the depth profile of the oxygen distribution in $Ge_{33}As_{12}Se_{55}$ films. We therefore investigate these issues in this paper.

2. Experiments

High quality $Ge_{33}As_{12}Se_{55}$ films were deposited by our unique ultrafast laser ablation method. A detailed description of the laser ablation system and deposition parameters can be found in our previous paper [5]. A 2.0 μm thick film deposited onto a 100 mm diameter silicon wafer was cut into smaller pieces, and then annealed in various pressures and temperatures. XPS spectra were collected under a vacuum of $\sim 10^{-10}$ Torr, where a monochromatic Al Kα X-ray ($h\nu$ = 1486.6 eV) at a power of 250 W was used as the excitation source. High-resolution spectra were recorded using a pass energy of 20 eV and a step of 0.1 eV. Carbon was selected as the internal reference and the binding energies of C 1s line was referenced at 285.0 eV. For the depth profile measurements, an Ar ion beam with an energy of 5 KeV was used to etch the films with an etching rate of 6 nm/s. By removing the Shirley baseline and fixing the doublet separation, the spectra were fitted with as few peaks as possible using XPSpeak 4.1 software until the (χ^2 value, which measures the goodness of the fit, reached a minimum.

3. Results and discussion

Fig. 1 shows Se 3d spectra of as-grown and annealed films and the bulk. Clearly the binding energy of the as-grown film decreases to that of the bulk with increasing annealing temperature. To quantitatively understand the evolution of Se clusters in the film, we decomposed Se 3d spectra by fixing the d-orbital separation at 0.85 eV [6,7]. We found that we could decompose the XPS spectra very well using three doublets to fit all the spectra. Roughly we sorted them into three types: Se-related, partly Ge(As)-related and full Ge(As)-related. The high energy wing in Fig. 1 is associated with the Se–Se–Se Structures. With decreasing binding energy, the decomposed peaks were assigned to partly and fully Ge(As)-related in sequence due to the fact that the negative shift of the bonding energy increases with the decrease of neighboring atom electro-negativity from Se(2.48) to As(2.18) and Ge(2.01) [1,6]. The decomposed 3d spectra are also shown in Fig. 1 as dotted lines.

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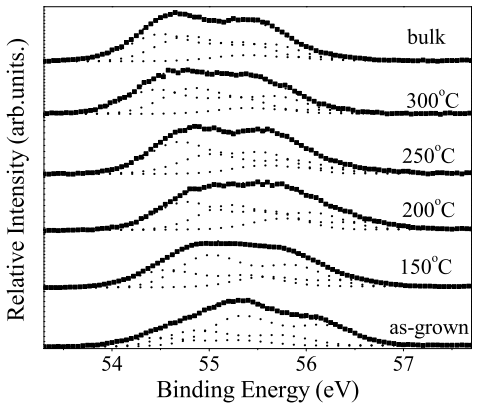

Fig. 1. Se 3d spectra of the as-grown, annealed film and bulk, the square dots are the experimental data and the dots line are the decomposed results.

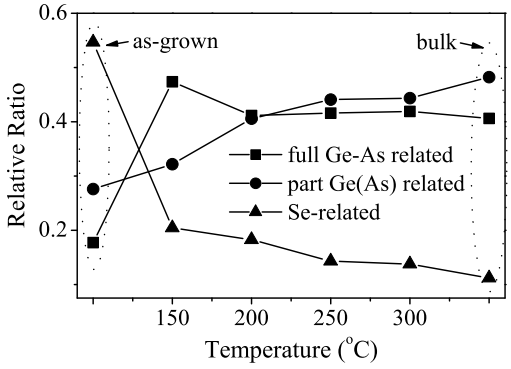

Fig. 2. The relative area ratio of three doublets in Fig. 1. The lines are drawn as guides for the eyes.

When the as-grown film was annealed, Se rebonded with those elements with low electro-negativity, leading to the decrease of the bonding energy with increasing annealing temperature.

The integrated areas for these three doublets as a function of the annealing temperature are plotted in Fig. 2. The large Se-related area ratio in the as-grown film suggests the existence of a large number of Se–Se–Se Structures. Due to expansion, the plume temperature at the substrate will be low [8], close to the glass transition temperature (T_g) of Se around 40–60 °C. Therefore Se atoms/ions can be easily condensed into amorphous rings or the chain molecular structures [1], resulting in the large Se-related area ratio. However, even the minimum annealing temperature 150 °C is much higher than T_g of Se, so these Se rings or chains can be broken by heating, allowing the Se to partly or fully coalesce with Ge or As. With increasing annealing temperature, coalescence could be expected to an increasing degree, and some of the broken Se served as a link between different structural units like $AsSe_{3/2}$ and $GeSe_{4/2}$, leading to the observed change of the part and full Ge(As)-related area ratios in Fig. 2.

We found that Ge and As 3d XPS spectra of both the as-grown and annealed films show clear peaks which can be assigned to Ge- or As-related oxides (the results are not shown here). These could originate from the residual oxygen in the deposition chamber or annealing oven and would saturate the dangling bonds on the surface of the films. To further confirm the oxidation behavior on the surface of the sample annealed at 150 °C for 15 h under 20 mTorr, we measured the etching time dependence of oxygen 1s spectra. The peak at 531 eV is strong on the surface but almost completely disappears after 15 s etching, indicating that the oxygen could react with the material and extend to deep layer below the surface.

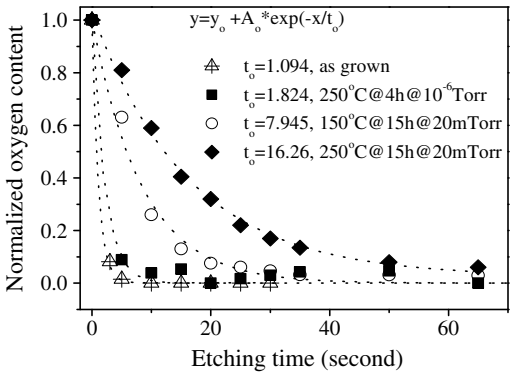

Fig. 3. Normalized depth profile of oxygen distribution in $Ge_{33}As_{12}Se_{55}$ films under several different processing conditions.

In total, we measured the depth profiles for four samples with different processing conditions, that are as-grown, 150 and 250 °C annealing samples for 15 h under 20 mTorr, and 250 °C annealing sample for 15 h under 1×10^{-6} Torr, respectively. For each sample, we normalized the integrated area of each O 1s spectrum after etching by that before etching. Fig. 3 displays the depth profile of oxygen distribution in $Ge_{33}As_{12}Se_{55}$ films under several different processing conditions. We found that, regardless of the annealing temperature and pressure, the normalized distribution of oxygen content can be well fitted by first order exponential decay function, $y = y_o + A_1 \cdot \exp\left(-\frac{x}{t_o}\right)$, where y_0 is offset, A_1 being amplitude and t_0 being decay constant. The critical thickness of the oxidized layer estimated by the decay constant and etching rate is 6.5, 11, 48 and 98 nm, respectively, for the as-grown, 250 °C annealing sample for 4 h under 1×10^{-6} Torr, and 150 and 250 °C annealing samples for 15 h under 20 mTorr.

4. Conclusion

In summary, we measured the XPS 3d spectra of as-grown and annealed films and bulk of $Ge_{33}As_{12}Se_{55}$. We found that, with increasing annealing temperature, Se clusters in the as-grown film break down and coalesce with Ge or As. On the other hand, both Ge and As 3d spectra show that the oxidized process occurs in as-grown and annealed films. The oxygen distribution along the normal direction of the films can be well fitted by the first order exponential decay function. The critical thickness of the oxidized layer is therefore derived for the films annealed under various conditions.

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