Antimony germanium sulphide amorphous thin films fabricated by chemical vapour deposition

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Abstract

Antimony germanium sulphide (Sb-Ge-S) amorphous thin films have been directly fabricated on both silica-on-silicon and commercial glass substrates by means of chemical vapour deposition. These Sb-Ge-S films have been characterized by micro-Raman, scanning electron microscopy and energy dispersive X-ray analysis techniques. Analysis results for these amorphous films indicate the composition of Sb-Ge-S can be varied by changing the deposition temperatures. The quality of these Sb-Ge-S amorphous thin films gives them high potential for the chalcogenide optical waveguide and device applications.

Keywords

Antimony germanium sulphide, thin films, chemical vapour deposition

Introduction

Thin amorphous chalcogenide films are very interesting materials because their diverse active properties allow their application as integrated planar optical circuits, as well as for memory and other optoelectronic applications [1-3]. The preparation of chalcogenide thin films can be performed by techniques which include thermal evaporation [4], sputtering [5], laser ablation [6], sol-gel [7], spin coating [8], and

chemical vapour deposition (CVD) [9-11]. In particular, the CVD technique has now proven to yield high quality germanium sulphide planar waveguides [11]. Germanium sulphide can easily incorporate antimony sulphide to form stable ternary glasses within a large glass forming region [12]. In addition, Sb-Ge-S glass has a higher refractive index and non-linearity than germanium sulphide glass [13], therefore, Sb-Ge-S amorphous thin films would be very useful for a number of active integrated optical circuit applications including spectral broadening and supercontinuum generation (SC) [14].

Germanium sulphide amorphous films have been successfully fabricated by using the reaction between germanium tetrachloride ($GeCl_4$) and hydrogen sulphide (H_2S) in our previous study [11]. In this paper, we report on the use of antimony pentachloride ($SbCl_5$) which will be used to react with H_2S to form antimony sulphide directly by the CVD technique. Moreover, by introducing $GeCl_4$ and $SbCl_5$ precursors together to react with H_2S would be able to form Sb-Ge-S amorphous thin films, which was the initial motivation for this research work.

Apparatus and experimental methods

The CVD apparatus for Sb-Ge-S amorphous thin film deposition is shown in Figure 1. In this process, Sb-Ge-S amorphous thin films with variable compositions can be achieved at the temperatures ranging from 120°C to 400°C. This is a hot-wall CVD process under atmospheric pressure, in which a horizontal quartz tube reactor (25mm O.D. x 500mm long) is heated in a tube furnace. The reactive gas, H_2S, and the carrier argon gas for $GeCl_4$ and $SbCl_5$ are delivered through the mass flow controllers (MFC) at the flow rate in the range of 50 ml/min-150 ml/min.

The thermodynamics and kinetics of the reaction between $GeCl_4/SbCl_5$ and H_2S determine the efficiency of the CVD process at a given reactant concentration and flow rate. No literature information is available for the kinetics of this reaction. However, a thermodynamics analysis of the formation of GeS_2 through the reaction between $GeCl_4$ and H_2S has been reported in our previous study [11]. The following thermodynamics analysis will concentrate on the reaction of formation of Sb_2S_3:

$$2SbCl_5 + 3H_2S \leftrightarrow Sb_2S_3 + 6HCl + 2Cl_2$$

which becomes increasingly favoured at high temperature. The Gibb's free energy of reaction (ΔG_r), which determines the equilibrium constant, can be calculated from the difference between sums of the Gibb's free energies of formation (ΔG_f) of the products and reactants [15]:

$$\Delta G_r = \Sigma \Delta G_{f,\ products} - \Sigma \Delta G_{f,\ reactants}$$

The equilibrium constant can be determined from $\Delta G_r = -RT \ln(K)$ where R is the gas constant and T is the temperature in Kelvin. As the temperature is increased, the equilibrium constant becomes larger (see Table 1), favouring the formation of Sb_2S_3. Non-stoichiometry is possible for antimony sulphide, which is not considered here. Nonetheless, as the temperature is increased, this analysis suggests that the reaction should also be increasingly favoured for antimony sulphide with a stoichiometry that is close to 1.5, which agrees with the energy dispersive X-ray (EDX) analysis.

Results and discussion

The thermal properties of Ge-Sb-S glasses studied by Takebe *et al* [16] suggest the glass transition temperatures (T_g) of these glasses would be in the range of 150-450°C and proportional to the content of germanium in the glass composition. Therefore, the

deposition temperatures of Sb-Ge-S amorphous thin films by the CVD techniques were selected in the range of 120-400°C in this research.

Sb-Ge-S amorphous thin films with the variable compositions have been successfully deposited on both silica-on-silicon and Schott N-PSK58 glass with the coefficient of thermal expansion (CTE) of 15.1 $x10^{-6}$/K, which provide the better thermal expansion compatibility [11], within the temperature range between 120°C and 400°C. Scanning electron microscopy (SEM) technique has been applied to study the morphology of Sb-Ge-S amorphous thin films. The SEM micrographs of cleaved edge of the Sb-Ge-S thin films on silica on silicon and Schott N-PSK58 glass substrates are shown in Figure 2. They show bubble and crack free thin films, free of any obvious inhomogeneity. As expected, the higher temperature of the CVD reaction, the greater the content of germanium was found in the Sb-Ge-S thin film. Energy dispersive X-ray (EDX) analysis has also been applied to determine the composition of Sb-Ge-S thin films and the results are summarized in Table 2. From the EDX results, the sulphur contents in all samples were in the similar range (59.3% - 61.6%). However, about 20.5% antimony and 17.9% germanium were formed in Sb-Ge-S thin film when the deposition temperature was selected at 400°C. As the deposition temperature decreased from 400°C to 120°C, the antimony content increased to about 37.7% while the germanium content decreased to about 2.5%. By changing the deposition temperatures, it would be feasible to control the composition of Sb-Ge-S thin films.

We use micro-Raman to characterize the composition and phase structure of Sb-Ge-S thin films deposited by the CVD process. The micro-Raman used is RENISHAW Ramascope which is equipped with a CCD camera. A 633nm He-Ne laser was used to excite the sample and the Raman shift spectrum was measured from $600cm^{-1}$ to $100cm^{-1}$ with a resolution of $1cm^{-1}$. These Raman spectra are shown in Figure 3 which

also agrees with those in the reference [16] although the intensities in Raman shift spectra of Sb-Ge-S thin films were different due to the thickness of the samples and the experimental conditions. In sample R96, the Sb-Ge-S thin film deposition took place at 400°C and about 17.9% germanium was formed in the film. The main Raman shift peak was found at about 330cm^{-1} that was influenced by the main peak of GeS_2 at 342cm^{-1}. On the other hand, in sample R102, the deposition formed at 120°C and only about 2.5% germanium formed in the film, the Raman shift peak was dominated by Sb_2S_3 at about 300cm^{-1}. However, from these Raman spectra, amorphous phases of the Sb-Ge-S thin films have been demonstrated.

Conclusion

Sb-Ge-S amorphous thin films deposited both on silica on silicon and Schott N-PSK58 glass substrates have been successfully fabricated by chemical vapour deposition (CVD). These Sb-Ge-S amorphous thin films have been characterized by micro-Raman, SEM and EDX techniques. The composition of Sb-Ge-S thin films can be varied by changing the deposition temperatures. These results show this CVD fabrication technique has a great potential in optoelectronics, particularly as waveguides for optical integrated circuits applications. Currently, we are working on these planar thin films to perform the rib waveguides and ring resonator structures by using the focused ion beam technique.

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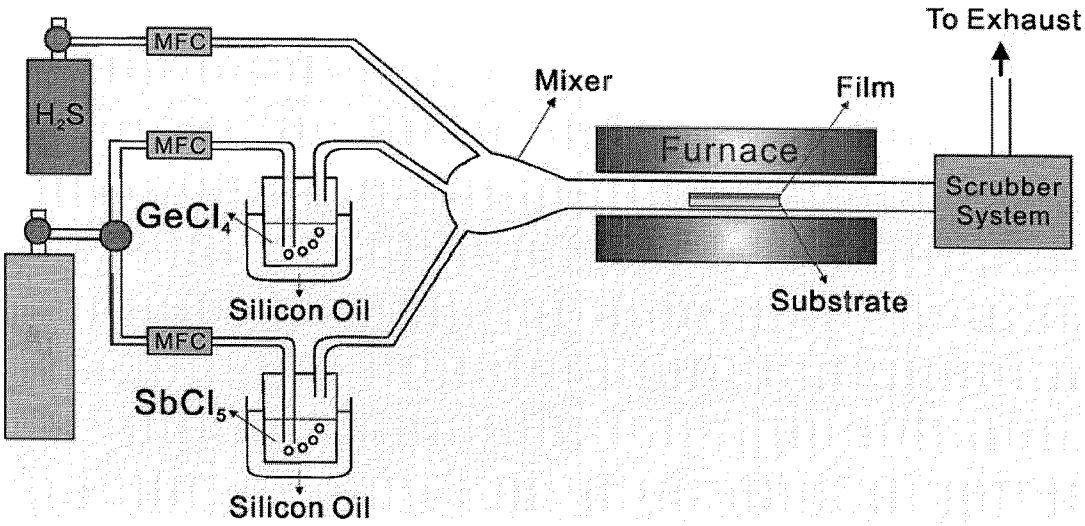
Fig. 2 *SEM micrographs of Sb-Ge-S thin films deposited on silica on silicon (left) and Schott N-PSK58 (right) substrates*

Fig. 3 *Raman spectra of Sb-Ge-S thin films deposited on Schott N-PSK58 substrates at the temperatures ranging from 120°C to 400°C*

Table 1 *Feasibility of the reaction of $SbCl_5$ and H_2S to form Sb_2S_3*

Table 2 *Summary of Sb-Ge-S thin films fabricated by CVD (R96-R102)*



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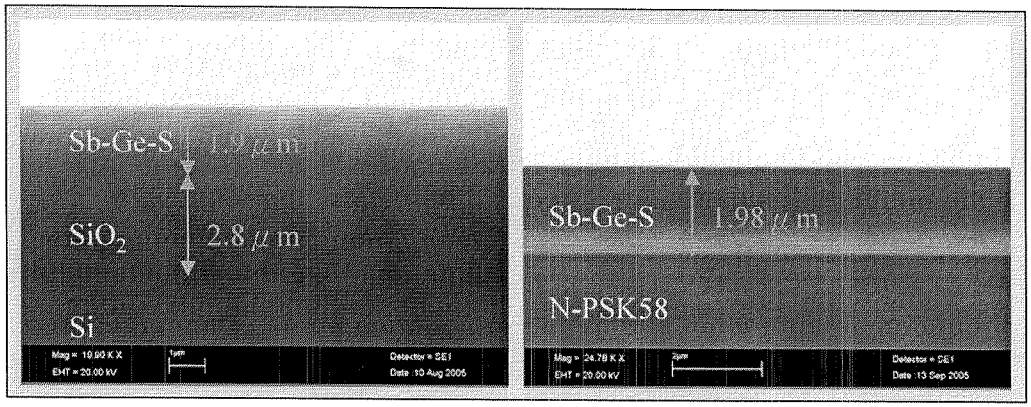

Fig. 2 *SEM micrographs of Sb-Ge-S thin films deposited on silica on silicon (left) and Schott N-PSK58 (right) substrates*

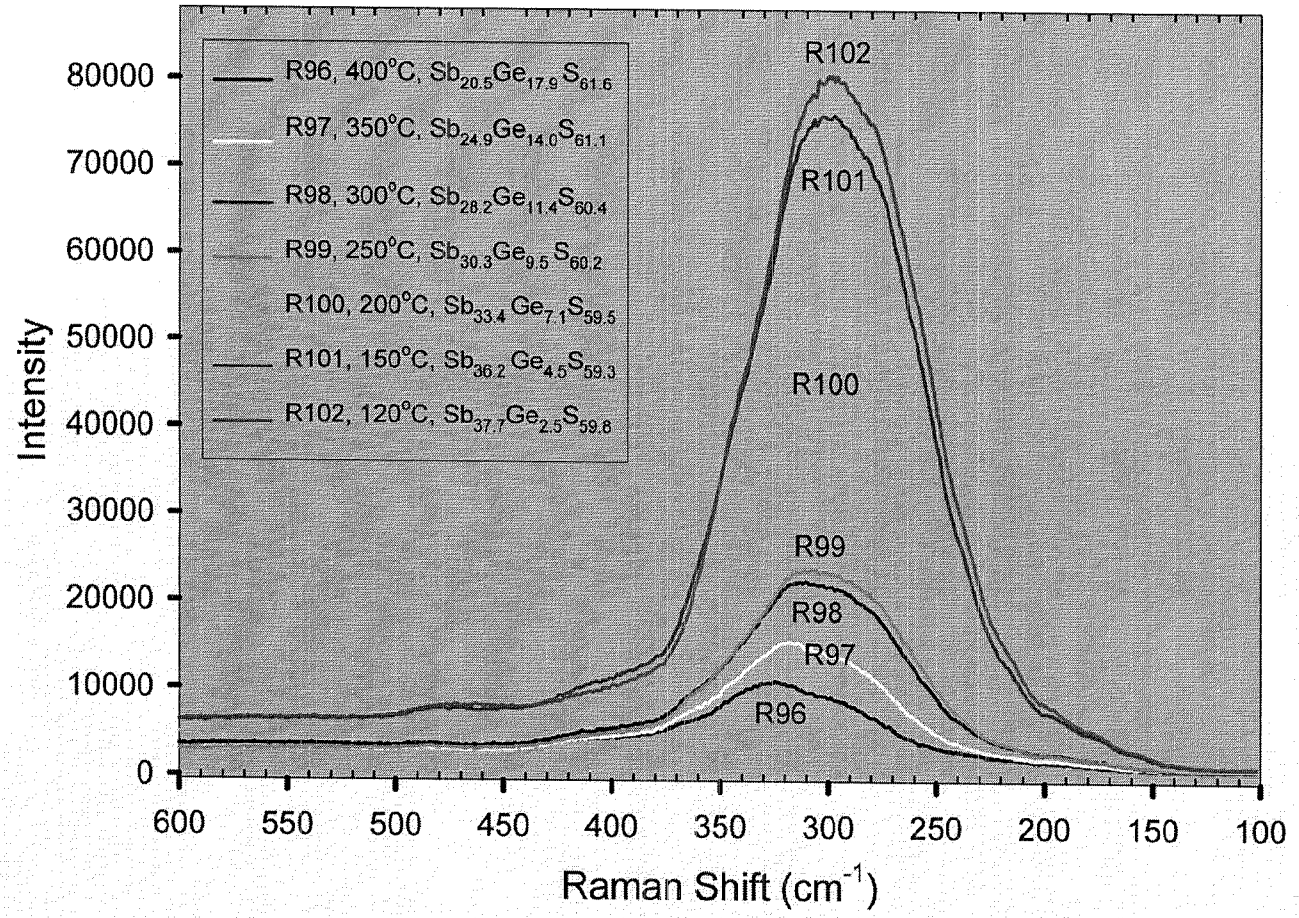

Fig. 3 *Raman spectra of Sb-Ge-S thin films deposited on Schott N-PSK58 substrates at the temperatures ranging from 120°C to 400°C*

	Room Temp.	500K	800K
ΔG_f (kJ/mol), Cl_2	0	0	0
ΔG_f (kJ/mol), HCl	-93.295	-97.158	-99.452
ΔG_f (kJ/mol), Sb_2S_3	-140.293	-136.844	-125.146
ΔG_f (kJ/mol), H_2S	-33.329	-40.179	-45.694
ΔG_f (kJ/mol), $SbCl_5$	-328.73	-288.697	-230.822
ΔG_r (kJ/mol), Reaction	45.396	-21.861	-123.132
K, equilibrium constant	1.098×10^{-8}	189.132	1.035×10^{8}

Table 1 *Feasibility of the reaction of $SbCl_5$ and H_2S to form Sb_2S_3*

Batch No.	Substrates	Temp. (°C)	Thickness (μm)	SEM-EDX
R96	N-PSK58	400	1.182	$Sb_{20.5}Ge_{17.9}S_{61.6}$
R97	N-PSK58	350	1.985	$Sb_{24.9}Ge_{14.0}$ $S_{61.1}$
R98	N-PSK58	300	1.590	$Sb_{28.2}Ge_{11.4}S_{60.4}$
R99	N-PSK58	250	1.677	$Sb_{30.3}Ge_{9.5}S_{60.2}$
R100	N-PSK58	200	2.563	$Sb_{33.4}Ge_{7.1}$ $S_{59.5}$
R101	N-PSK58	150	3.824	$Sb_{36.2}Ge_{4.5}$ $S_{59.3}$
R102	N-PSK58	120	3.905	$Sb_{37.7}Ge_{2.5}$ $S_{59.8}$

Table 2 *Summary of Sb-Ge-S thin films fabricated by CVD (R96-R102)*