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Thermal dissolution of Ag(Cu) in amorphous $Ge(S_x\ Se_{1-x})_2$ system

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ABSTRACT

Thermally induced solid state reaction of Ag(Cu) into thin $Ge(S_x\ Se_{1-x})_2$ films with $x=0$, 0.1, 0.4 and 1.0 was investigated using a step by step technique in order to design films with exact Ag(Cu) concentrations for applications in integrated IR optical devices. A thin film of Ag(Cu) was deposited on top of the host $Ge(S_x\ Se_{1-x})_2$ films followed by annealing in vacuum at constant temperature, which resulted in homogeneous films of good optical quality. The variation in Ag(Cu) concentration in the films ranged between 5 and 35 at.%. The kinetics of the diffusion and dissolution of metal in the host films was measured by optically monitoring the change in thickness of doped chalcogenide during consecutive thermal annealing steps. The kinetics studies revealed that the thermal dissolution rate of the Cu is greater than that of Ag. Optical UV–VIS transmission spectra of chalcogenide glass layers, undoped and thermal doped by Ag(Cu), were measured to establish the optical properties of the films. The spectra were analyzed using the technique proposed by Swanepoel and the results show that the addition of metal increases the absorption coefficient in the power-law regime and consequently the optical gap decreases and the refractive index increases. The amorphous character of the films was checked by X-ray diffraction which confirmed the amorphous structure of all Ag(Cu) – Ge – S – Se thin films.

1. Introduction

Amorphous germanium chalcogenides glasses have motivated many investigations due to their potential for application in integrated optical devices, especially in the infrared spectral region [1,2]. Since they show high transmission in this region of the spectrum, they are particularly suited for active and passive IR devices [3,4]. A further important step towards implementation as photonic devices is the introduction of lateral optical confinement in order to fabricate wave guiding devices. This can be done by laser beam writing, standard wet etching techniques [5], or local metal doping. This last technique is based on diffusive doping process, which has the fundamental advantage that it produces relatively smooth index profiles.

The dissolution and diffusion of some metals, such as Ag or Cu, into chalcogenide glasses have been widely studied and used to fabricate micro-optics devices [6,7]. This can be done by using the thermal diffusion (TD) technique [8]. In this technique, the matter flux along the concentration gradient is enhanced by overcoming the energy barrier via heating of the host material. Such thermal diffusion is a common strategy in the semiconductor technology and it is used for the development of impurity concentration profiles in integrated circuits. The diffusion process changes the structure of the chalcogenide hosting material particularly at the nano-scale [9]. Different reaction products form and different diffusion kinetics will dominate in each compound of the whole range of chalcogenide systems, while mechanisms for these processes have been proposed and discussed in the literature [10]. A unifying model for understanding the formation and nature of the new structure is lacking. Hence, experimental data in this area are helpful for understanding the "TD" process in chalcogenide films. The advantage of the "TD" is that a large amount of metal can be driven into the chalcogenide glasses; this alters the optical constants. The kinetics of the "TD" process is very important because the speed with which the metal ions migrate into the chalcogenide film governs the required exposure to heat. Various techniques have been developed to measure the kinetics of "TD". One of these techniques consists of monitoring the transmittance or reflectance of the multilayer combination [11].

In the present paper, we have analyzed in detail the influence of step-by-step Ag(Cu) thermally doping, on the optical properties of amorphous $Ge(S_x\ Se_{1-x})_2$ chalcogenide films with $x=0$, 0.1, 0.4 and 1.0. In a previous paper [12], we have reported on the effect of sulfur substitutions on optical, electrical and structure properties of $Ge(S_x\ Se_{1-x})_2$ system.

2. Experimental

The $Ge(S_xSe_{1-x})_2$ alloys with $x=0$, 0.1, 0.4 and 1.0 host films were prepared by using a well-established vacuum evaporation technique.

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The bulk chalcogenide glasses used as an evaporation source were prepared from the constituent pure elements by the usual melt quenching technique. The bulk glass preparation process has been described elsewhere [12]. The host films were prepared on cleaned silicate glass substrates under vacuum of about 1×10^{-4} Pa. The deposition parameters were kept constant so that comparison of results could be made under identical conditions. Subsequently, different thicknesses of silver (Ag) or cupper (Cu) layer were deposited on the top of the chalcogenide host films for each composition by a thermal evaporation. The host films were thermally activated doped by consecutive dissolving of Ag(Cu) layers, resulting in films of very good optical quality. This method was carried out by annealing the Ag or Cu coated films in vacuum oven at 180 °C until the metal films diffused inside the chalcogenide films.

Using energy-dispersive X-ray technique (EDX) on a Joel Jsm-5410 scanning electron microscope, the Ag(Cu) concentration was determined. The error in EDX measurements is about ±3%. In addition, a different EDX measurement points were used to confirm clearly the composition homogeneity of the host and thermally doped films. The Ag(Cu) concentration of the prepared samples was ranged between 5 and 35 at.%. The metal–chalcogenide films prepared by this method are less likely to crystallize than the films prepared from melt quenching bulk metal–chalcogenide samples [13].

X-ray diffraction (XRD) technique was used to confirm the diffusion of the Ag(Cu) thin film and the amorphous structure of the doped films. The XRD study was performed on X-ray diffraction of type (Diano Corporation) using Co Kα as a source. The X-ray tube was operated at 45 kV and 9 mA diffraction pattern from 2θ = 4 to 80° which were recorded by a step scan method.

The optical transmission spectra of the films were recorded with a double beam Shimadzu UV–VIS spectrophotometer in the spectral rang 200–1100 nm. The homogeneity of the doped thin-film samples was clearly confirmed by the corresponding spectral dependence of transmission, where no shrinkage of the interference fringes was observed.

3. Results

3.1. The kinetics of the thermal-diffusion of Ag(Cu) into $Ge(S_xSe_{1-x})_2$ films

The kinetics of the TD reaction between Ag or Cu and a-$Ge(S_xSe_{1-x})_2$ host films, in a conventional sandwich structure, are measured by optically monitoring the change in thickness of the doped chalcogenide film. In this experiment, the TD process is performed by consecutive heating of the sample, for discrete periods of time. After each period of heating the optical transmission spectrum of the bilayers sample is measured using the spectrophotometer. The transmission curves of Ag (Cu) thermally doped in $Ge(S_{0.4}Se_{0.6})_2$, as an example of the host films, are shown in Fig. 1. The TD reaction developed a homogeneous film with a very good optical quality. Moreover, as the Ag or Cu dissolves in the host film, the metal layer becomes thinner and finally the metal layer completely diffused; eventually the film becomes transparent. For $Ge(S_{0.4}Se_{0.6})_2$ host and thermally doped films, the experimental data of the overall transmission at constant wavelength through the multilayer structure are fitted by the function as shown in Fig. 2. The average rate of change of optical transmission is different for each curve, a slightly more rapid change occurring for the Cu metal curve.

The thickness of the thermally doped layer is determined qualitatively from the evolution of the optical transmittance during the process [11]. The measured kinetics curves (i.e. doped layer thickness vs. annealing time) for the $Ge(S_{0.4}Se_{0.6})_2$ host film are shown in Fig. 3. Experimental data were fitted using a nonlinear function, as it is shown in figure. The constant values of the function are $a=528.54$, $b=-3.073$, $x_o=74.08$ for Ag doping and $a=695.98$, $b=-2.11$, $x_o=63.21$ for Cu doping. This function suggests that the diffusion of metal atoms through the host film following a sigmoidal behavior. Two stages of the diffusion process are appeared with different kinetics for Cu comparing with Ag.

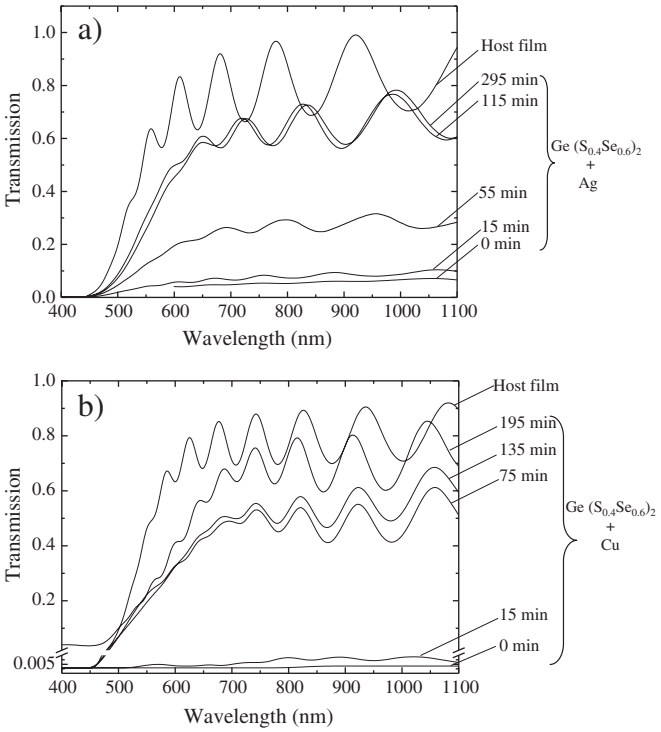

Fig. 1. Evolution of the optical transmission for a thermal-doped thin film (a) by Ag and (b) by Cu.

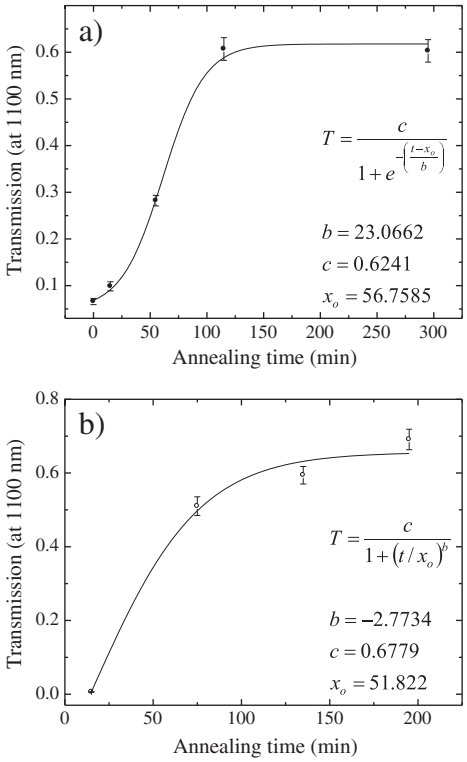

Fig. 2. Optical transmission (measured at 1100 nm) of the bilayer $Ge(S_{0.4}Se_{0.6})_2$ during TD (a) by Ag and (b) by Cu. Error bars are influenced by Fabry–Perot oscillation of the transmission data, see Fig. 1. The solid line is a fit to the experimental points.