

Silver-doped germanium sulphide glass channel waveguides fabricated by chemical vapour deposition and photo-dissolution process

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Abstract

Germanium sulphide glass thin films have been fabricated by chemical vapour deposition directly on commercial glass substrates. Silver (Ag)-doped channel waveguide structures were then prepared in a three step process, first channels were patterned in photo-resist, next a Ag thin film was deposited on the patterned waveguide by thermal evaporation, and finally the silver ions were doped into germanium sulphide glass by a photo-dissolution process. The refractive index of germanium sulphide increased by about 0.02 through the photo-dissolution process. The loss of the channel waveguides measured at 632.8 nm was 0.63 ± 0.05 dB/cm.

Keywords

Germanium sulphide glass, channel waveguides, chemical vapour deposition, Ag photo-dissolution

1. Introduction

A range of photo-induced phenomena exhibited by chalcogenide thin films enables them to be utilized in a variety of optical applications [1]. Among these phenomena optically-induced diffusion and dissolution (OIDD), also known in the literature as photo-doping or photo-dissolution, is particularly interesting Metals such as Ag, Zn,

Cu or Cd doped into amorphous chalcogenide semiconductors has been extensively studied by many researchers [2-14] because of both fundamental and technological interests. In the bi-layer or multi-layer metal/chalcogenide structure, light illumination induces fast migration of metal atoms into the glass structure. Amorphous $\text{Ag/As}_{33}\text{S}_{67}$ and $\text{Ag/Ge}_{30}\text{S}_{70}$ films have recently been shown to be useful materials for fabrication of phase gratings and other diffractive optical elements with relief nanostructures [15-17]. There are also other related phenomena in Ag-rich chalcogenide glasses e.g. in ternary systems Ag-As-Se, Ag-As-S, Ag-Ge-S, which exhibit so-called photoinduced surface deposition of metallic Ag, i.e. photoinduced segregation of fine particles on the glass surface [18-23]. Furthermore, it was found that silver-containing chalcogenide film exhibits reversibility in optical writing and thermal erasing of the Ag patterns [24].

Another potential application is optical data storage, where the recording of information takes place in thin films, with stoichiometric composition such as AgAsS_2 [25] and Ag-As(Ge)-S systems [26, 27]. Such glasses are potentially applicable to phase-change optical recording through a laser induced, phase transition between amorphous and crystalline states [28]. Generally, such a transition can be induced by light exposure to perform either irreversible or reversible recording depending on the energy and intensity of light. The glasses of Ag-Ge-S, Ag-Ge-Se, Ag-As-S, and Ag-As-Se systems belong to the so-called super ionic conductors [29] and this quality has been demonstrated to be beneficial in, for example, cell device applications [30].

The OIDD process allows the preparation of chalcogenide films with the silver content in a wide concentration range. A silver concentration increase leads to a red

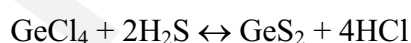
shift of the optical absorption edge and the refractive indices increase with increasing silver content [4]. However, there is still no publication concerning waveguide fabrication by using this OIDD process. Therefore, an attempt to fabricate Ag-doped chalcogenide glass channel waveguides by using the OIDD process has been initiated.

In this study, germanium sulphide glass thin films were deposited on glass substrates by the chemical vapour deposition (CVD) process we have previously reported [31]. Channel structures were then formed by the photo-lithography process by patterning in photoresist, after which a 10nm thick layer of Ag was deposited on the germanium sulphide glass film by thermal evaporation. This was followed by the photo-dissolution process, after which the residual photo-resist was removed by acetone. Ag-doped germanium sulphide glass channel waveguides were demonstrated with a loss of 0.67 ± 0.05 dB/cm at 632.8 nm.

2. Apparatus and experimental methods

2.1 Germanium sulphide planar waveguide prepared by the CVD process

Germanium sulphide planar waveguides have been fabricated by means of a chemical vapour deposition process developed in our previous research work [31]. This promising procedure, illustrated schematically in Figure 1, has provided a direct way to form chalcogenide planar waveguides for a variety of optoelectronic applications. In the process, we synthesize high purity germanium sulphide through reaction of GeCl_4 and H_2S at temperatures of $450^\circ\text{C} - 600^\circ\text{C}$:



This forms a germanium sulphide glass thin film directly on a variety of substrates. We have chosen a Schott N-PSK 58 glass slide which is a high quality commercial

borosilicate/ borophosphate glass as a substrate material. With a thermal expansion coefficient of $15.1 \times 10^{-6} / \text{K}$, this provides a good match of thermal property with the deposited film. The reactor used in the experiment is horizontal quartz tube within a wire wound tube furnace capable of reaching $1500 \text{ }^\circ\text{C}$. The reactive gas, H_2S , and the carrier gas for GeCl_4 , argon, are delivered through the mass flow controllers which provide $\pm 1 \text{ ml/min}$ accuracy. In the small scale experiment illustrated we were able to deposit a 2 micron thin film in about 4 minutes. The optimum temperature, $500 \text{ }^\circ\text{C}$, was set to be between the glass transition temperature (T_g) and the onset of crystallization temperature (T_x) of the desired product.

2.2 Silver coating by thermal evaporation

A silver thin film provides the metallic layer for subsequent photo-dissolution. These Ag coatings were prepared by thermal evaporation deposition directly on the GeS_2 film. An Edward coater E306A was used to carry out this deposition process. The raw material, Ag wire, with a purity of 99.99 %, was obtained from Agar Scientific. The Ag wire was wound around the tungsten filament and the germanium sulphide glass thin film was situated just above the Ag source in the vacuum chamber. Deposition took place under vacuum with a pressure about $1 \times 10^{-6} \text{ mbar}$. The deposition was controlled by a film thickness monitor (gold coated quartz sensor, Z value = 16.7 and density = 10.5 for Ag) at a rate of 0.1 nm/sec . In this way we were able to deposit a 10nm thick Ag layer in about 100 seconds.

2.3 Photo-dissolution process

The OIDD mechanism suggested by D. Goldschmidt and P.S. Rudman [32], postulates that light must be absorbed in the Ag metal which generates hot electrons.

These electrons travel a distance on the order of their mean-free path (several hundred Å). These hot electrons, surmounting the barrier between the chalcogenide and the Ag, enter the chalcogenide behind Ag^+ ions. Therefore, the generated electrostatic attraction enhances the transfer of Ag^+ to the chalcogenide. Inside the chalcogenide, transport of Ag^+ occurs either by thermal diffusion or is enhanced by the electric field at the doped-undoped interface. In our experiments we tested this hypothesis by taking steps to minimize any thermal effect.

The set-up for the Ag photo-dissolution process is shown in Figure 2. A white light (150W tungsten-halogen lamp) was used as the source, passing through a heat absorbing infrared filter (Schott KG1 type glass disc, 3 mm thickness, 350 - 700 nm short-pass filter) to illuminate the Ag layer coated on germanium sulphide glass thin film. The infrared filter was used to eliminate the possibility of thermal diffusion and temperature measurements indicated that there was less than a 2 °C rise in the temperature with the infrared filter in place. It is however possible for the OIDD process to be conducted without the infrared filter. The illumination time for the Ag to completely dissolve into the germanium sulphide glass film varied from one to several hours depending on the thickness of Ag layer.

2.4 Refractive Index measurement of Ag doped germanium sulphide glass film

The method suggested by Swanepoel [33] was used to measure the refractive index (n) and film thickness of germanium sulphide glass waveguides, and the refractive index of Ag doped germanium sulphide glass waveguides. According to Swanepoel's method of creating the upper and lower envelopes of the transmission spectrum with

interference fringes, the refractive index was calculated by the following equation (Eq. 1).

$$n = \sqrt{N + \sqrt{N^2 - s^2}} \quad (\text{Eq. 1})$$

where
$$N = 2s \frac{T_M - T_m}{T_M T_m} + \frac{s^2 + 1}{2}$$

$$s \text{ (the refractive index of the substrate)} = \frac{1}{T_s} + \sqrt{\frac{1}{T_s^2} - 1}$$

T_s = transmission of substrate at the wavelengths

T_M = value of transmission maximum at the wavelengths of the upper envelopes

T_m = value of transmission minimum at the wavelengths of the lower envelopes

The accuracy to which the wavelength can be measured is $\pm 1\text{nm}$. The maximum absolute accuracy of T_M and T_m is ± 0.001 .

Also, if n_1 and n_2 are the refractive indices at two adjacent maxima (or minima) at wavelengths λ_1 and λ_2 , using the basic equation for interference fringes (Eq. 2):

$$2nd = m\lambda \quad (\text{Eq. 2})$$

where m is an integer for maxima and half integer for minima, the thickness (d) is given by Eq. 3.

$$d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)} \quad (\text{Eq.3})$$

In order to study the refractive index change of a Ag doped germanium sulphide film, a 42 nm thick Ag layer was deposited on the germanium sulphide glass planar waveguide by thermal evaporation and this was followed by the photo-dissolution process. The refractive index of the Ag doped germanium sulphide film was determined by the same single transmission method and compared with the original germanium sulphide glass thin film prior to doping with silver (Figure 3). The transmission spectra of the germanium sulphide glass planar waveguide and Ag-doped germanium sulphide planar waveguide were measured by a Varian Cary 500 Scan UV-VIS-NIR Spectrophotometer at the resolution of 1 nm. By using Swanepoel's method, we can calculate the refractive index and the thickness of the germanium sulphide glass planar waveguides as a function of wavelengths. The results are summarized in Table 1. The refractive index of the germanium sulphide glass film, measured by the single transmission method, agrees with the previous measurement made by a prism coupling technique [31]. The refractive index changes (Δn) between Ag doped germanium sulphide glass and germanium sulphide glass waveguides were shown in the Figure 4. The refractive index change of 42 nm thick Ag doped into germanium sulphide glass film has been increased by the photo-dissolution process and the values are in a range between 0.18 and 0.14 and vary with wavelength.

In order to reduce the refractive index change (Δn) between Ag doped germanium sulphide glass and surrounding un-doped germanium sulphide glass, a thinner 10nm thick Ag coating was used to create a germanium sulphide glass planar waveguide using a process identical to that previously used. As the results shown in Figure 4, the

Δn has been reduced to a range from 0.02 to 0.04 again as a function of the wavelengths.

3. Fabrication of Ag doped channel waveguides

From the previous work on silver diffusion into planar films, we now have confidence that the Ag photo-dissolution process can be applied to locally increase the refractive index of a germanium sulphide thin film and thereby define channel waveguides in the glass. We fabricated Ag doped germanium sulphide glass channel waveguides achieved by the photolithography process, then deposited a 10 nm Ag layer on the germanium sulphide glass film. This was followed by the photo-dissolution process, and finally removal of residual photo-resist. The fabrication procedures are shown schematically in the Figure 5.

The Ag doped germanium sulphide glass channel waveguides were initially evaluated by an optical microscope with a magnification of 20 and 40. As the photographs show in Figure 6, Ag doped germanium sulphide channel waveguides with a width of 5 μm have been fabricated by the CVD, photolithography, thermal evaporation, and photo-dissolution process.

4. Waveguide attenuation measurement

The attenuation of Ag doped germanium sulphide channel waveguides was measured by the fibre coupling technique with a He-Ne laser at the wavelength of 632.8 nm. The image was taken with a CCD camera and converted to the pixel intensity along the length and the attenuation was fitted by linear regression. As the results show in

Figure 7, the attenuation of Ag doped germanium sulphide glass channel waveguides was 0.67 ± 0.05 dB/cm at 632.8 nm.

5. Conclusion

Ag-doped germanium sulphide glass channel waveguides have been fabricated by means of the CVD, photo-lithography, thermal evaporation, and photo-dissolution process. The refractive index of the planar waveguides have been studied by the single transmission technique and the refractive index of Ag doped germanium sulphide glass planar waveguide can be increased and controlled by the doping level of Ag content. The attenuation of Ag doped channel waveguides have been demonstrated with the loss of 0.67 ± 0.05 dB/cm at 632.8 nm. The preliminary results indicate the potential for applications in optoelectronics, especially for channel waveguides in integrated optic circuits.

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Table 1 *Values of λ , T_M , T_m , T_s , and s for the calculation of refractive index and film thickness of germanium sulphide glass planar waveguides.*

λ (nm) (± 1 nm)	T_M (± 0.001)	T_m (± 0.001)	T_s (± 0.001)	S (± 0.001)	n	d (μm)
770	0.857	0.716	0.908	1.563	2.075 ± 0.004	
741	0.860	0.712	0.909	1.559	2.093 ± 0.003	2.12
713	0.856	0.708	0.907	1.568	2.105 ± 0.004	2.24
687	0.851	0.705	0.908	1.563	2.102 ± 0.005	2.26
663	0.847	0.701	0.908	1.563	2.105 ± 0.005	2.25
642	0.843	0.697	0.908	1.563	2.107 ± 0.003	2.18
621	0.838	0.693	0.908	1.563	2.109 ± 0.005	2.10
603	0.832	0.688	0.908	1.565	2.117 ± 0.003	2.17
585	0.828	0.683	0.907	1.568	2.126 ± 0.003	2.17
569	0.823	0.678	0.908	1.563	2.129 ± 0.004	2.16
553	0.818	0.674	0.907	1.568	2.137 ± 0.005	2.20
539	0.813	0.668	0.907	1.568	2.141 ± 0.003	2.17
525	0.807	0.663	0.907	1.568	2.148 ± 0.005	2.27
512	0.802	0.659	0.907	1.568	2.152 ± 0.005	
500	0.796	0.654	0.907	1.568	2.156 ± 0.005	

Film thickness from calculation: $2.19 \pm 0.05 \mu\text{m}$

Table 1 Values of λ , T_M , T_m , T_s , and s for the calculation of refractive index and film thickness of germanium sulphide glass planar waveguides.

Figure No: 1

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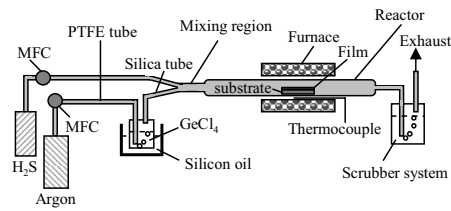


Fig. 1 Schematic diagram of CVD system used for thin film deposition

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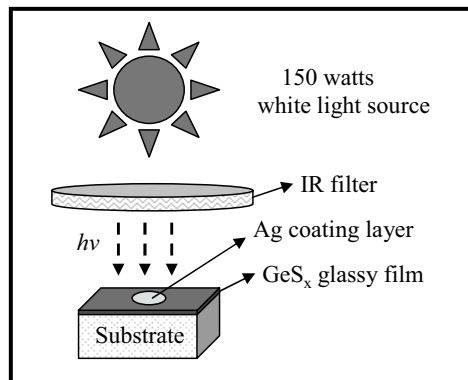


Fig. 2 Set-up for Ag photo-dissolution process

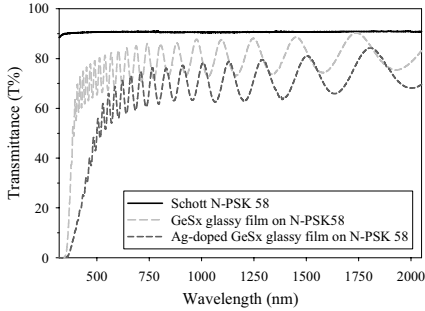


Fig. 3 *UV-VIS-NIR spectra of germanium sulphide glass and Ag doped germanium sulphide glass planar waveguides*

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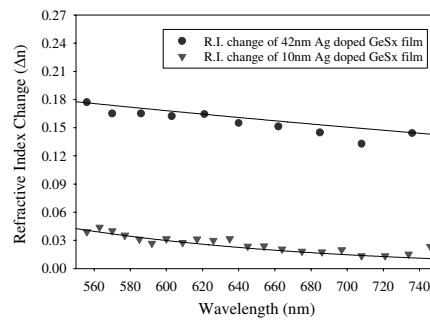


Fig. 4 Refractive index change (Δn) between Ag doped germanium sulphide glass and germanium sulphide glass planar waveguides

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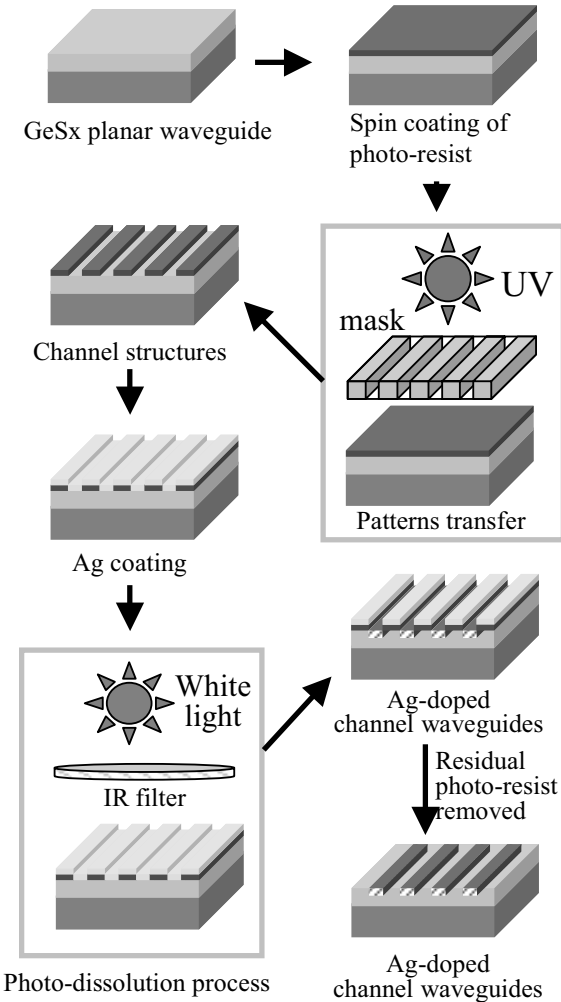


Fig. 5 Fabrication procedures for Ag doped germanium sulphide glass channel waveguides

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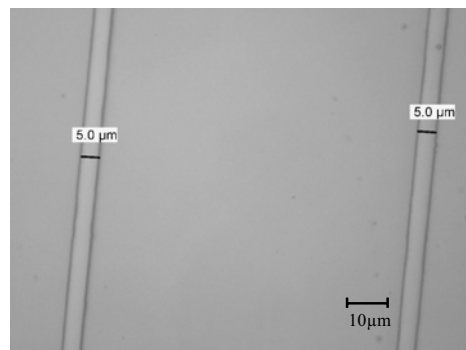


Fig. 6 *Ag doped germanium sulphide glass channel waveguides*

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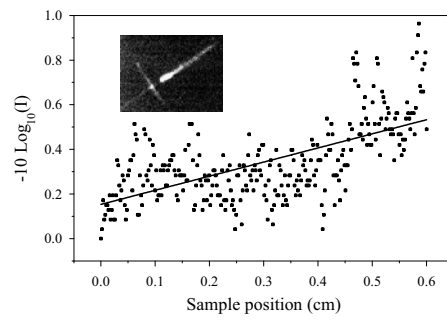


Fig. 7 Attenuation of Ag doped germanium sulphide glass channel waveguides at 632.8 nm, as determined from a least square fit to the experimental data of the CCD image is 0.63 ± 0.05 dB/cm