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Systematical changes in diffraction efficiencies through Ag-photodoping into amorphous GeSe thin films

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ABSTRACT

It is well known that the phenomenon of Ag-photodoping into amorphous (a-) chalcogenide film depends on film thickness (d). Herein, we report that the effects of Ag-photodoping into a-GeSe thin films exhibit a systematical change dependent on d using a holographic exposure (HeCd laser) and the measurement of diffraction efficiency (η) in real time. The η-kinetics of Ag-photodoping in the sample structure of an a-GeSe/Ag/p-type Si substrate is divided into two steps. A *photodarkening-dominant process* related to the generation of valence-alternation pairs (VAPs) in the chalcogenide explains the first step while a *doping-dominant process* accounts for the second step. In particular, we confirmed that the d-dependencies of the η-kinetics are classified into 3 groups: (A) $d < 2d_P$; (B) $2d_P \leqslant d < 4d_P$; (C) $d > 4d_P$, where d_P indicates the penetration depth of the HeCd laser. In group A, the Ag-doping process occurs simultaneously with the darkening process. In group C, the η-kinetics results from the darkening process only. Contrarily, in group B, the η-kinetics exhibits a sharp distinction between the photodarkening process and the Ag-doping process, and in particular, η_M increases almost linearly with an increase in d.

1. Introduction

Amorphous (a-) chalcogenide thin films currently have many potential applications in optics, optoelectronics, and chemistry due to inherent photoinduced changes ranging from photodarkening, photorefraction, and photopolymerization to photocrystallization, photoexpansion, and photodoping [1–7]. In particular, a-chalcogenides are very promising materials for use in fiber optics and waveguide-based devices in integrated optics, given their exceptional transparency in the infrared region, including the telecommunication wavelength of 1.31 and 1.55 μm [8]. In the photodoping phenomenon, the above optical bandgap light illumination ($h\nu > E_{OP}$) induces a dissolution and a fast photostimulated migration (or diffusion) of metallic positive-ion species (Ag, Cu, and In) into chalcogenides [9,10]. In addition, the migration into non-illuminated regions of the chalcogenide is generally very small [11,12]. The Ag-photodoping causes a structural change in the chalcogenides and eventually a change in etching solubility. In particular, Ag-doped chalcogenide films act as a negative-type resist for an alkaline-etching development.

There are a number of reports explaining the kinetics of photodoping [9–18]. It is a well-known property that Ag atoms are more concentrated at the outer edges of the illuminated region than in the central region. This edge-sharpening effect has been explained using the alleged surface diffusion model [17] and the photoinduced and electron-induced chemical modification process [19,20]. In addition, Kolobov and Elliott [2] reported a model to account for the transfer of Ag^+ into the chalcogenide by treating the system as a metal solid electrolyte. In this model, they concluded that, for photodoping, the light should be absorbed in the vicinity of the doped–undoped chalcogenide interface and that the role of light at the interface is to mainly lower the energy barrier, thereby enhancing Ag flow. However, as even light that is hardly absorbed can still cause photodoping, Lis and Lavine [10] proposed another suggestion that the light must be absorbed into the metal according to the internal photoemission model [21].

Until now, we have reported on the Ag-photodoping phenomena into chalcogenides in the following publications: the magnitudes of Ag-doping in the Ag/a-Sb_2S_3/Si and Ag/a-AsGeSeS/Si systems by illumination with a 325 nm HeCd laser and their wet-etching selectivities [12,22]; the possibility of Ag-photodoping into several crystalline chalcogenide compounds and their kinetics [23]; and the influence of substrate and structure on the Ag-photodoping effect into a-GeSe thin films as 2 types of sample

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structures (Ag/*a*-SeGe/substrate and *a*-SeGe/Ag/substrate) [18]. From a series of experimental results, we concluded that the substrate-dependence for Ag-photodoping could be explained by the diffusion of minority carriers in the films and the change of the magnitude and direction within the internal fields generated at the film interfaces [18]. In addition, we proposed that the magnitude of Ag-photodoping in the structure of the *a*-chalcogenide/Ag/substrate depends strongly on the photodarkening-dominant process in the chalcogenide, related to the generation of valence-alternation pairs (VAPs) [18,22,24]. The aim of the present work is to confirm that the Ag-photodoping effect into *a*-GeSe thin films exhibits a systematical change dependent on the film thickness and to explain the kinetics.

2. Experimental procedures

Details of the *a*-$Ge_{25}Se_{75}$ bulk preparation were described previously by Lee et al. [3,18]. Ag and *a*-$Ge_{25}Se_{75}$ thin films were successively thermally deposited on a p-type Si (100) substrate at a deposition rate of approximately 0.1–0.3 nm/s, under a vacuum of $\sim 2 \times 10^{-6}$ Torr. Ag thickness was fixed to be approximately 10 nm and *a*-GeSe films were varied in thickness (d) ranging from 100–400 nm. Fig. 1 shows the schematic diagrams for the holographic exposure and real-time diffraction efficiency (η) measuring systems and for interference effects in the chalcogenide film by two equal beams. A rectangular stage with a mirror and a sample holder was designed capable of precisely controlling the incident diffraction angle ($0° < \theta < 80°$) and sample rotation angle ($0° < \gamma < 180°$), in which γ rotation needs to fabricate two-dimensional photonic and quasi-photonic crystals using a multiple exposure holographic method [18,25].

A 442 nm HeCd laser ($h\nu = 2.80$ eV) was utilized as the light source for the holographic exposure and a 632.8 nm HeNe laser ($h\nu = 1.96$ eV) was used to measure the η-variation in real time. The Ag-photodoping kinetics was indirectly evaluated by monitoring the η-variation. In this work, holographic exposure was carried out at $\theta \sim 8°$ and irradiance by the HeCd laser beam measured on the sample was maintained at 10 mW/cm^2, while irradiance of the HeNe laser utilized to measure the η-variation was maintained below 1 mW/cm^2 in order to minimize the influence of the probing beam on the sample. Dotted lines shown in the right part of Fig. 1(a) represent the wavefronts of two plane waves with Λ as the period of gratings (constructive interference) formed in the chalcogenide film by the Ag-photodoping effect. The value of Λ ($\theta = 8°$) calculated by the relationship between Λ and θ, $\Lambda = \lambda/(2\sin\theta)$, is approximately 1.59 μm. In general, η is defined by the relationship: $(I_1/I_0) \times 100\%$, where I_0 and I_1 are the irradiances of zeroth and first order diffraction beams reflected from the sample, respectively.

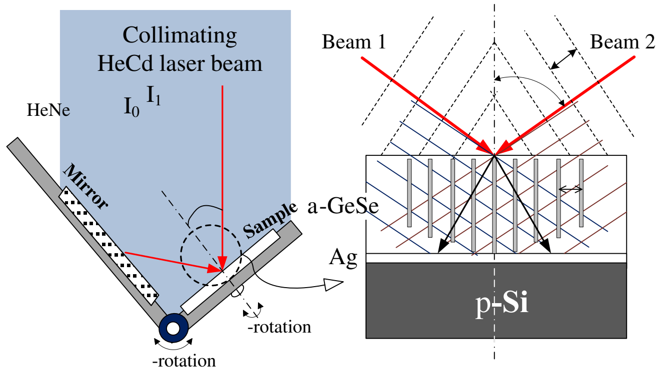

Fig. 1. Schematic diagrams for holographic exposure and real-time η measuring systems (left) and for the interference effect in the chalcogenide film by 2 equal beams (right): θ = incident angle; γ = sample rotation angle; I_0 and I_1 = irradiances of 0th and 1st order diffraction beams; and Λ = grating period.

3. Results

Fig. 2 shows the logarithmically scaled plot of η vs. exposure time (t) for a sample of 250-nm-thick *a*-GeSe/Ag/*p*-type Si substrate. The η-kinetics to reach the maximum η (η_M) appeared to be comprised of two steps, photodarkening-dominant process and doping-dominant process. An abrupt increase in the first derivative of η vs. t, $d\eta/dt$, was observed at the boundary between two steps. In case of the sample of Fig. 2, the quantities of $d\eta/dt$ at the boundary increased from $\sim 5 \times 10^{-6}$%/s to $\sim 2.2 \times 10^{-4}$%/s.

As shown in Fig. 2, the η-value increased very slowly and almost linearly for the first step ($t < t_D$), but increased exponentially for the second step ($t_D < t < t_M$). Eventually, η reached η_M but decreased with little saturation. The symbol t_M represents the minimum exposure time to achieve η_M, and t_D and η_D indicated the exposure time and efficiency at the boundary between two stages, respectively. For the sample in Fig. 2, the values of η_D (t_D) and η_M (t_M) were evaluated to be approximately 0.0374 (4500 s) and 0.690 (9180 s), respectively. The η-kinetics for the samples (*a*-GeSe/Ag/Si substrate) with different thicknesses of *a*-GeSe (d = 100, 150, 200, 250, 300, and 400 nm) is shown in Fig. 3.

4. Discussion

As shown in Fig. 3, the η-kinetics for the samples of d = 150 nm and 200 nm was similar to that for d = 250 nm (Fig. 2), in which both darkening and doping-dominant processes appear for reaching η_M. In particular, the darkening-dominant regions for the samples with d = 150, 200, and 250 nm showed a tendency to be systematically expanded with an increase in d. Contrarily, there was no darkening-dominant region in the case of the sample of d = 100 nm. In addition, the darkening-dominant region for the samples of d = 300 and 400 nm was so long that the doping-dominant region was not observed despite sufficient exposure time. Fig. 4 shows the variations of t_M, t_D, η_M, and η_D as a function of *a*-GeSe thickness.

As shown in Fig. 4(a), exposure times, t_M and t_D, are exponentially prolonged with an increase in d. The η_M value increases almost linearly with d with an approximate slope of 2.7×10^{-3}%/nm,

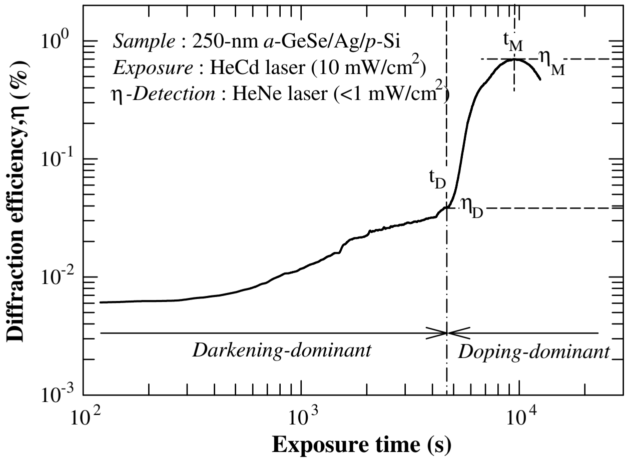

Fig. 2. Log-scaled plot of η vs. t for a sample of 250-nm-thick a-GeSe/10-nm-thick Ag/p-type Si substrate: t_M = minimum exposure time required to achieve η_M; and t_D = exposure time at the boundary between the darkening and doping dominant processes. For this sample, η_D (t_D) = 0.0374 (4500 s) and η_M (t_M) = 0.690 (9180 s).