



Beynəlxalq Konfrans "Fizika-2005" International Conference "Fizika-2005" Международная Конференция "Fizika-2005"

7 - 9

İyun
June 2005
Июнь

№184
page 698-702
стр.

Bakı, Azərbaycan

Baku, Azerbaijan

Баку, Азербайджан

ELECTRICAL AND OPTICAL CHARACTERISTICS OF Ag/CdTe THIN FILM STRUCTURES

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Effect of Ag diffusion on electrical, optical and structural properties of Ag/CdTe structures have been investigated. In the range of 280-420°C the effective coefficient of thermal diffusion (D_t) and photodiffusion (D_{ph}) are described as $D_t = 1.9 \times 10^5 \exp(-1.60/kT)$ and $D_{ph} = 8.7 \times 10^3 \exp(-1.36/kT)$. The acceleration of Ag diffusion under illumination was tentatively attributed to photoionization of Ag increasing the interstitial flux of silver. Ag/CdTe structures exposed to annealing were characterized by X-ray diffraction (XRD), I-V, C-V, conductivity-temperature and optical transmission measurements. In XRD patterns of annealed Ag/CdTe structures, besides the intensive (111) peak of cubic CdTe, the weak peaks of Ag_2Te phase are also present. The temperature dependence of conductivity and the absorption spectra of annealed Ag/CdTe structures showed the energy levels 0.13 eV and 0.10 eV respectively and nature of these levels were discussed.

INTRODUCTION

The CdTe thin film is promising base material for a solar cell owing to its nearly optimum band gap and high absorption coefficient. Elements of the group I (Cu and Ag) are an everpresent residual impurity in CdTe. Moreover they are used as contact material for fabrication of CdTe/CdS solar cells and metal/CdTe interfaces play an important role in cells. Cu and Ag are known as substitution acceptor impurities in Cd positions (Cu_{Cd} or Ag_{Cd}). In addition, they are reported to be incorporated also as interstitial donors and the diffusion coefficient of interstitial ions is known to be very high [1,2]. Besides, Cu and Ag is able to form complexes with V_{Cd} and V_{Te} vacancies. These impurities are considered to be principal component responsible for the degradation of CdTe/CdS cells due to their ability to diffuse through the CdTe film to the cell junction. In the photoluminescence spectra of Ag-doped CdTe peaks at 1.491 eV and 1.590 eV are attributed to a donor-acceptor pair between cadmium-vacancy (V_{Cd}) and Ag in interstitial position (Ag_i) [3]. A photoemission study of Ag/CdTe interfaces prepared by evaporation of Ag on the room-temperature, surface of CdTe showed a significant

concentration of dissociated Te in reacted form with the overlayer Ag metal [4]. According to Wolf et al. [5] the diffusion profiles of Ag and Cu introduced by implantation of radiotracers Ag^{111} and Cu^{67} in bulk CdTe directly reflect the distribution of intrinsic defects, such as V_{Cd} and Cd_i . Influence of illumination on diffusion in Cu/CdTe thin film structures and photostimulated degradation of characteristics of CdTe(Cu)/CdS cells was reported in [6]. According to our knowledge, photostimulated diffusion in Ag/CdTe thin film structures has not been reported yet. The present work reports data on thermal and photostimulated diffusion in Ag/CdTe thin film structures and influence of Ag diffusion on structural, electrical and optical characteristics of Ag/CdTe structures and CdTe films.

EXPERIMENTAL

CdTe films of thickness 1-5 μm were deposited on glass substrates by closed-space sublimation (CSS) technique. The substrate and source temperature were 600 and 390°C respectively. The as-prepared CdTe films were n- or p-type and at high resistivity ($\rho = 10^4 - 10^7 \Omega cm$). Thermal annealing

of n-type CdTe at 400°C for 1h in air resulted in the conversion of conductivity type from n- to p-type. Ag/CdTe structures were fabricated by electron-beam evaporation of Ag films of thickness 5-50 nm on CdTe surface at room temperature. The thickness of Ag film was measured during evaporation by using Deposition Controller (Inficon, Leybold).

Films and structures were characterized using X-ray diffraction (XRD), resistivity, optical transmission, current-voltage and capacitance-voltage measurements. The XRD data of samples were taken using Rigaku D/Max-111C diffractometer with $\text{CuK}\alpha$ radiation over the range $2\theta = 10-70^\circ$. Optical transmission spectra of CdTe and Ag/CdTe structures (after diffusion annealing) were measured in the wavelength range of 300-1100 nm and 2-25 μm at room temperature by using a ‘Lambda-2’ (Perkin-Elmer) spectrometer and ‘Matson 1000’ Fourier transform infrared (FTIR) spectrometer respectively. In-Ga alloy was used as ohmic contact to CdTe layers. Etch treatment of the p-type CdTe surface using $\text{HNO}_3 - \text{H}_3\text{PO}_4$ solution prior to applying the contact material has been explored to achieve a p^+ -surface layer and thus low resistance contact on CdTe.

For examination of the effect of heat treatment in dark (thermal diffusion) and under illumination (photodiffusion) on structural, electrical and optical properties, two Ag/CdTe structures, closely located on common substrate were exposed to sequential cycles of treatments in dark (thermal annealing) or under illumination (photo-annealing) by a tungsten-halogen lamp in vacuum (about of 1.3 Pa) at fixed temperatures (280, 320, 370 and 420°C) [7,8]. Ag/CdTe structures serving as the unilluminated samples shielded from light were located adjacent to the illuminated samples. In these experiments, the temperatures of the surface of Ag/CdTe structures under illumination and in the dark were measured using a copper-constantan thermocouples attached to the surfaces. After Ag diffusion, the residue of silver on CdTe surface was removed by etching in HNO_3 . Then resistivity measurements by using two- or four-probe technique were carried out after each cycle of treatment at room temperature. Dependence of resistance on duration of annealing in dark and under illumination (R-t curve) was used for estimation of effective diffusion coefficient (D) of Ag in CdTe films [9,10]:

$$D = (h^2/4) \{d(R/R_0)/d(t^{0.5})\}^2 \quad (1)$$

Here R_0 and R is resistance before diffusion annealing ($t=0$) and after diffusion for t respectively, h is thickness of CdTe film.

The net donor or acceptor concentration of the CdTe layer was measured by a C-V profiling technique. C-V measurement was carried out at 1 MHz using Ag/CdTe junction at room temperature.

RESULTS AND DISCUSSION

XRD patterns of CdTe film presented in figure 1a. showed that CdTe is polycrystalline in nature with a preferential orientation along (111) plane of the cubic

phase. XRD patterns of Ag/CdTe structure exposed to thermal annealing at 400°C for 1h (Figure 1b.), showed, besides (111) peak of CdTe, yet two diffraction peaks at $2\theta = 38.9$ and 47.3° which can indexed to (040) and (004) of monoclinic Ag_2Te [11].

It should be noted that peaks related with Ag_2Te phase were also observed for Ag/CdTe structures exposed to photoannealing at 400°C. Formation mechanism of Ag_2Te phase can be attributed to reactive diffusion due to interaction of Ag with Te at Ag/CdTe interface. The dissociation of Te from CdTe film and subsequent reaction with the overlayer Ag diffusing into CdTe can result in formation of Ag-Te phase [4].

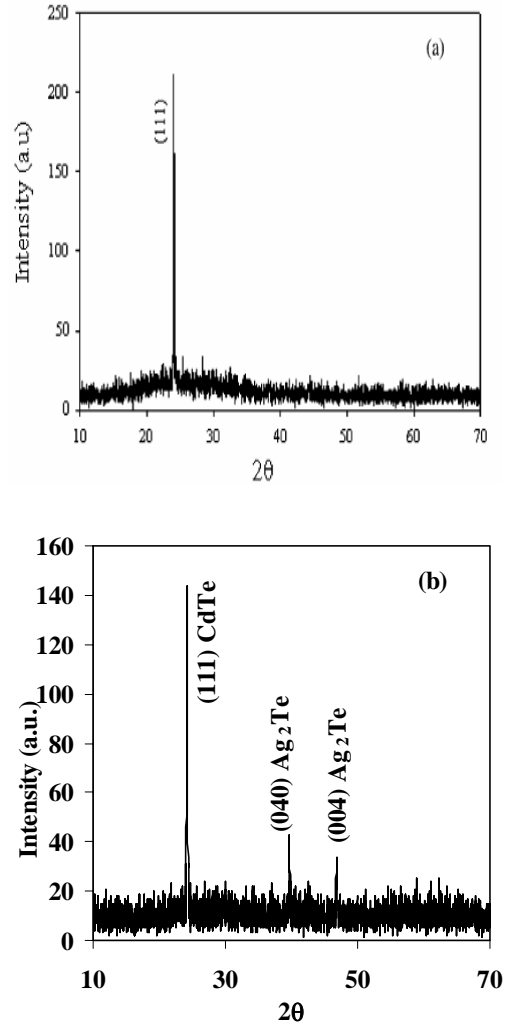


Figure.1. XRD pattern for (a) CdTe film (b) Ag/CdTe annealed at 400°C for 1h.

Figure 2 illustrates the absorption coefficient spectrum of CdTe film. Analysis of this curve shows a behavior expected for direct band semiconductor

$$\alpha^2 (h\nu)^2 = B(h\nu - E_g) \quad (2)$$

Here, $E_g = 1.49$ eV is energy gap of CdTe film and B is constant.

Figure 3 presents the dark current-voltage characteristic of Ag/pCdTe structure after thermal annealing at 400°C for 1h. It can be seen that I-V curve discovers the considerable rectification.

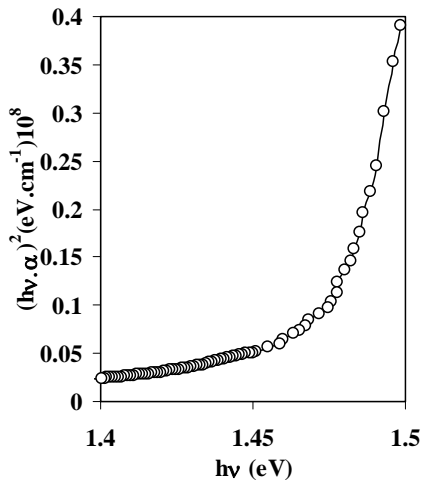


Figure 2. Absorption spectrum of CdTe film.

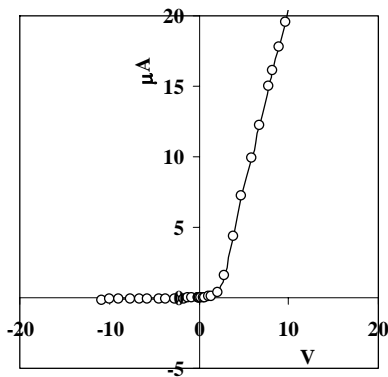


Figure 3. Dark current-voltage characteristic of Ag/CdTe structure exposed to photoannealing.

The barrier height obtained from the equation

$$\phi_b = (kT/e) \ln (A^*T^2/J_s), \quad (3)$$

gave $\phi_b = 0.83$ eV. Here A^* is the effective Richardson constant at 300K, k is the Boltzman constant (8.62×10^{-5} eV/K), e is the electronic charge and J_s is the saturation current density.

$J_s = 3.7 \times 10^{-8}$ A/cm² was determined from extrapolated values of the forward current density to zero voltage. The ideality factor β obtained from gradient

$$\beta = (e/kT) [dV/d(\ln J)] \quad (4)$$

varies from 1.9 to 10. However, in view of the non-ideal behavior of the Ag/CdTe structures value of ϕ_b is highly unreliable. Considerable deviation of the ideality factor from unity, indicates the presence of a large contribution from recombination and generation in the depletion region.

The capacitance – voltage data were analyzed by plotting C-V dependence (Figure 4). Barrier height (ϕ_b)_{cv} and ionized acceptor concentration (N) were obtained from intercept and the gradient

$$N = (2/\epsilon\epsilon_0 S^2) [d(C^{-2})/dV]^{-1} \quad (5)$$

Here ϵ is the dielectric constant (for CdTe $\epsilon = 10.2$), $\epsilon_0 = 8.85 \times 10^{-12}$ F/m, S is the area of junction surface. Calculated value of the barrier height is 0.70 eV and the acceptor concentration in CdTe is 1.4×10^{15} cm⁻³. The small difference of barrier height determined from I-V and C-V characteristics can be related with a high density of recombination centers at interface increasing the recombination current.

The heat treatment at 280-420°C was accompanied by decrease of resistivity of n-type CdTe film, whereas for Ag/pCdTe diffusion of Ag resulted in increase of resistivity of p-type CdTe. These data can be evidence of predominantly the donor behavior of Ag in CdTe films. Ag in interstitial position of CdTe lattice or (Ag_{Cd} - V_{Te}) complexes can be responsible for donor properties of silver.

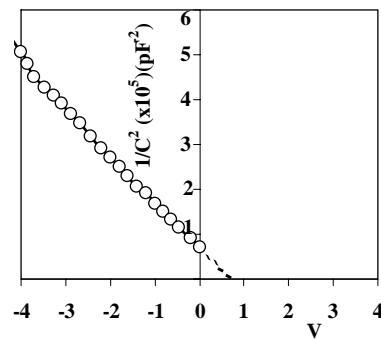


Figure 4. Capacitance versus reverse voltage characteristic of Ag/p-CdTe structure exposed to photo annealing

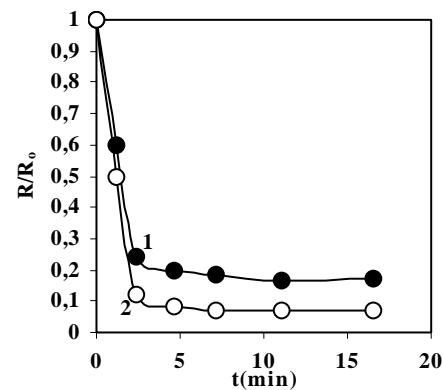


Figure 5. Resistance of n-CdTe(Ag) in dependency on annealing duration (1) in dark and (2) under illumination at 320°C.

Room temperature resistance studies of Ag/nCdTe structures exposed to sequential cycles of thermal (in dark) and photoannealing at fixed temperatures (280, 320, 370 and 420°C) showed that rate of decrease of resistance of n-type CdTe for photoannealing is higher than that of thermal

annealing. Data on resistance versus annealing duration for thermal and photoannealing of Ag/nCdTe at 320°C are showed in figure 5. It is seen that for both type annealing the increase of duration of annealing is accompanied by decreasing of resistance and then saturation of R-t curves. Data on the effective diffusion coefficient of Ag in n-type CdTe on temperature in the range of 280-420°C for thermal (D_t) and photostimulated diffusion (D_{ph}) are described as (Figure 6.)

$$D_t = 1.9 \times 10^5 \exp(-1.60/kT) \quad (6)$$

$$D_{ph} = 8.7 \times 10^3 \exp(-1.36/kT) \quad (7)$$

The activation energy for photostimulated diffusion (1.36 eV) is smaller than that of thermal diffusion (1.60 eV). The effective diffusion coefficient of Ag for photostimulated migration is larger than that for thermal diffusion by 4-6 times.

Ag similarly other impurities of group 1 (Cu, Au) migrates predominantly along grain boundaries of polycrystalline CdTe film with simultaneous diffusion into grains where migrates faster via interstitial as ionized donor [6,12,13]. The acceleration of Ag diffusion under illumination can be tentatively attributed to photoionization of Ag resulting in an increase in the fast migrating interstitial flux of silver [14]. In the case Ag/CdTe, migration of Ag into CdTe can be accompanied with reactive diffusion with formation Ag-Te phases. Higher values of activation energy for Ag in CdTe (1.60 and 1.36 eV for thermal and photostimulated diffusion respectively) in comparison with that for Cu in CdTe (0.33 and 0.20 eV, respectively) [6] can be explained by interaction of Ag with Te [4].

Figure 7 shows the conductivity-temperature dependence of n-type CdTe(Ag) film diffusion-doped by Ag at 400°C for 1h. The activation energy determined from low-temperature slop (30-145°C) is 0.13 eV.

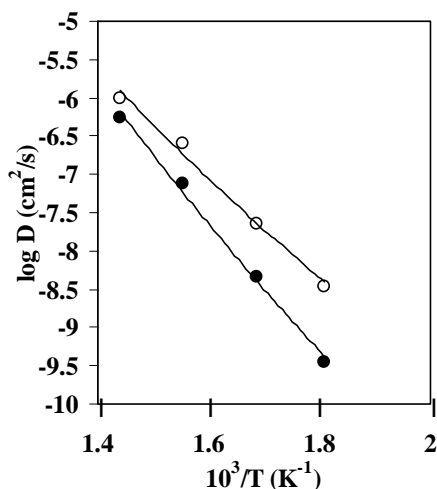


Figure 6. The temperature dependence of the effective diffusion coefficient of Ag in n-CdTe on (1) thermal and photodiffusion

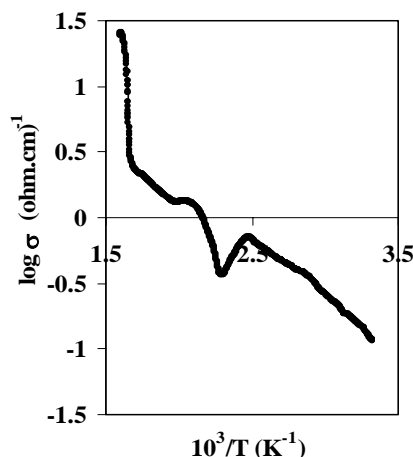


Figure 7. Dependence of conductivity of n-type CdTe(Ag) on temperature.

An abrupt decrease of conductivity above 145°C and subsequent increase of conductivity with slop about of 0.23 eV is observed. It should be noted that the temperature of the sharp change of conductivity (about of 145°C) is approximately coincides with a transform temperature of Ag_2Te (about of 140-150°C) [15]. Figure 8 illustrates the absorption spectrum of CdTe(Ag) film doped Ag diffusion at 400°C for 1h. The absorption edge (about 0.10 eV) is in the rough agreement with the low-temperature slop of 0.13 eV determined from σ -T curve (Figure.7).

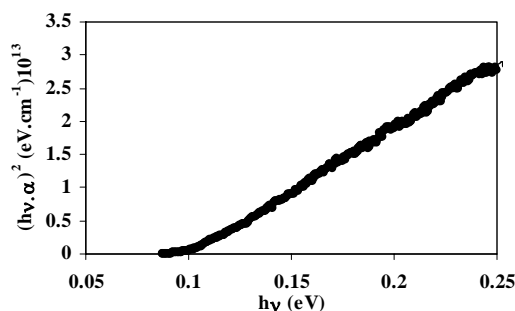


Figure 8. Absorption spectrum of CdTe(Ag) film.

These peculiarities observed in σ -T and α -h ν plots of Ag/CdTe structures after diffusion annealing can be tentatively related with the reactive diffusion of silver accompanied with formation of the narrow energy band Ag_2Te phases on interface region.

CONCLUSIONS

This study shows that the effective diffusion coefficient of silver in CdTe films at 280-420°C under illumination is larger than that without illumination by 4-6 times. This effect is attributed to increase of interstitial flux of Ag ions due to photo ionization. In addition, diffusion of Ag in CdTe structures discovers the reactive behavior with formation of Ag_2Te phases at interface region of Ag/CdTe structures.

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