

# Effect of Ion Bombardment on the Density of States of Valence Electrons in CdS Films

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**Abstract**—Cd nanofilms with a thickness of 10–12 Å are obtained by bombarding a CdS surface with Ar<sup>+</sup> ions. The obtained Cd–CdS nanofilm systems are shown to be promising for creating metal–insulator–semiconductor and semiconductor–insulator–semiconductor heterostructures and forming nanoscale barrier layers and hyperfine ohmic contacts on the semiconductor surface.

**Keywords:** electronic structure, CdS films, composition, distribution profile, sputtering, ion bombardment, nanoscale structure

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## INTRODUCTION

At present, CdS films find application in various sensors, photocells, emission cavities, and solar cells. Therefore, numerous studies have been devoted to the formation, morphology, composition, structure, and properties of CdS films (particles) and heterosystems based on them [1–7]. In addition, according to recent investigations, the nanoscale structures of these materials are promising for designing new solid-state electronics devices [8–11]. The use of semiconductor materials often requires continuous homogeneous metallic or semiconductor thin films with a thickness of ~10–50 Å to be formed on their surface. Such films are usually obtained by depositing atoms of the desired metal onto the semiconductor surface in ultra-high vacuum. However, the deposition of continuous homogeneous films with a thickness of  $d \leq 50$  Å is a challenging problem. Moreover, a thin oxide film forms between the deposited film and the substrate. In recent years, ultra-thin homogeneous layers have been most frequently obtained by low-energy ion implantation. In [12, 13], a new method was proposed to form nanocontacts on the surface of semiconductors by the example of Si(111) films. In this method, first, cobalt-silicide films with a thickness of 45–50 Å are formed by the high-dose ( $D = 5 \times 10^{16} \text{ cm}^{-2}$ ) implantation of Co<sup>+</sup> ions on the surface of Si in combination with annealing and, then, contacting metal (Al) atoms are deposited. CoSi<sub>2</sub> films have the properties of a metal ( $\rho = 3 \times 10^{-5} \Omega \text{ cm}$ ). Similar films with a complex

composition were obtained by the ion implantation of a GaAs and CaF<sub>2</sub> surface [14, 15].

Semiconductors coated with very thin metallic layers are promising for the creation of ohmic contacts, barrier layers, high-speed Schottky-barrier-based devices, and metal–insulator–semiconductor and semiconductor–insulator–semiconductor nanofilm heterostructures for microwave transistors and very-large-scale integrated circuits. However, there has been a lack of such studies on CdS films and samples. It should be noted that the main drawback of ion bombardment is that metallic films can only be obtained on the surface of binary materials with metal as a component.

The main goal of this work is to examine the formation of nanoscale structures on CdS surface layers under bombardment by Ar<sup>+</sup> ions with an energy of  $E_0 = 1–3$  keV in different doses and investigate their composition, structure, and electronic properties.

## EXPERIMENTAL

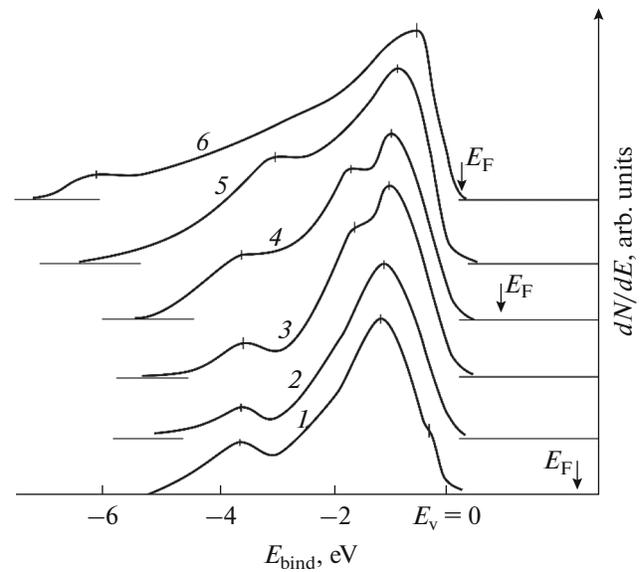
The objects of study were polycrystalline *n*-CdS films with a thickness of ~1 μm grown on the surface of SnO<sub>2</sub> glass by thermal evaporation in vacuum at a residual pressure of ~10<sup>-6</sup> mm Hg [2]. Ion bombardment and the deposition of atoms were performed perpendicular to the target in vacuum at a residual pressure of no worse than 10<sup>-6</sup> Pa. Auger electron spectroscopy, photoelectron spectroscopy, and high-

energy electron diffraction studies were carried out. The depth distribution profiles of atoms were determined by Auger electron spectroscopy combined with layer-by-layer etching by argon ions with an energy of  $E_0 = 2$  keV at an angle of  $5^\circ$ – $10^\circ$  to the sample surface.

## RESULTS AND DISCUSSION

Before ion bombardment, the CdS films were purified by heating at  $T = 1200$  K for 3–4 h. The surface concentration of oxygen was  $\sim 1$ – $1.5$  at %. Figure 1 presents the photoelectron spectra for well-purified CdS films bombarded by  $\text{Ar}^+$  ions with an energy of  $E_0 = 1$  keV in doses of  $D = 10^{14}$ – $10^{17}$   $\text{cm}^{-2}$ . The electron binding energy  $E_{\text{bind}}$  was plotted along the abscissa axis. The energy was counted from the top of the CdS valence band. The Fermi level  $E_F$  and its change under ion bombardment are shown by arrows. We chose the same vertical scale in all the curves such that the area under the curve was proportional to the quantum escape of electrons from the samples. The spectrum of the pure CdS film (curve 1) has features at binding energies of  $E_{\text{bind}} \approx -0.7$ ,  $-1.3$ , and  $-3.6$  eV. We can assume that the formation of the main maximum at  $E_{\text{bind}} \approx -1.3$  eV involves mainly Cd 5s electrons. The features at  $E_{\text{bind}} \approx -3.6$  eV can be caused by the excitation of electrons from the hybridized cadmium 5s and sulfur 3p levels and the feature at  $E_{\text{bind}} = -0.7$  eV, by the excitation of electrons from the surface states of the CdS films. Under ion bombardment, the main changes in the photoelectron spectrum occur starting with an ion dose of  $5 \times 10^{14}$   $\text{cm}^{-2}$ . The intensity of the main CdS peak somewhat decreases and a new feature arises nearby. An increase in the irradiation dose to  $D = 5 \times 10^{15}$   $\text{cm}^{-2}$  enhances this feature, somewhat reduces the main peak, and shifts its position by  $\sim 0.2$  eV toward higher energies. Simultaneously, the peak caused by the surface states disappears, the peak at  $E_{\text{bind}} \approx -3.6$  eV significantly decreases and broadens. At a dose of  $D = 10^{16}$   $\text{cm}^{-2}$  near  $E_{\text{bind}} \approx -1.5$  eV, one peak arises again instead of the two peaks and, at  $D = 5 \times 10^{16}$   $\text{cm}^{-2}$ , the photoelectron spectrum typical of metals is observed, which is confirmed by the coinciding  $E_F$  and  $E_v$  positions.

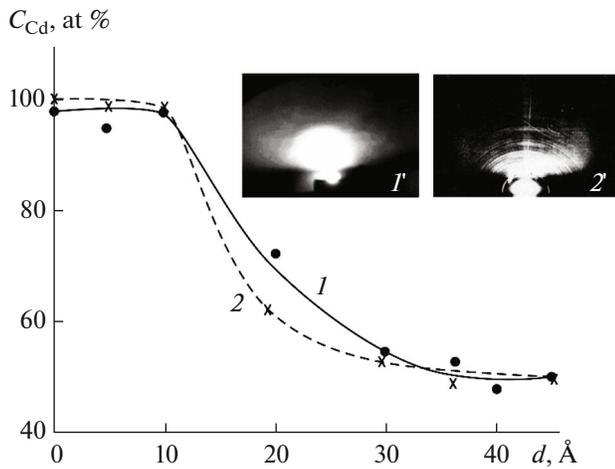
The dynamics of the photoelectron spectrum of CdS under bombardment by  $\text{Ar}^+$  ions can be explained using Auger electron spectroscopy data. In the range of  $D = (5 \times 10^{14})$ – $(5 \times 10^{15})$   $\text{cm}^{-2}$ , the peak typical of unbound sulfur atoms in the Auger spectra intensified. It is likely that, at these doses, sulfur atoms predominantly diffuse to the surface due to CdS decomposition. Consequently, the surface layers are enriched with S atoms and the surface layers, with Cd atoms. At low ion doses, separate nanocluster phases form on the sample surface. As the dose increases, the size of these phases increases and, at high doses ( $D \geq 10^{16}$   $\text{cm}^{-2}$ ), the boundaries of the neighboring phases overlap and a con-



**Fig. 1.** Photoelectron spectra recorded after bombardment of the CdS film by  $\text{Ar}^+$  ions with an energy of  $E_0 = 1$  keV in doses  $D$  of (1) 0 (pure CdS), (2)  $5 \times 10^{14}$ , (3)  $10^{15}$ , (4)  $5 \times 10^{15}$ , (5)  $10^{16}$ , and (6)  $5 \times 10^{16}$   $\text{cm}^{-2}$  (curves 5 and 6 are shown for the twofold magnification of  $dN/dE$ ).

tinuous fully disordered layer forms. Therefore, with an increase in  $D$  from  $5 \times 10^{14}$  to  $5 \times 10^{15}$   $\text{cm}^{-2}$ , the S concentration on the surface increases and the main CdS peak decreases and, due to the partial disordering of the surface, slightly shifts toward higher energies. At  $D = 5 \times 10^{15}$   $\text{cm}^{-2}$ , S atoms are desorbed from the surface layers; maximum (98–99 at. %) evaporation is observed at  $D = 5 \times 10^{16}$   $\text{cm}^{-2}$ . A further increase in  $D$  does not change the CdS composition and surface structure; i.e.,  $D = 5 \times 10^{16}$   $\text{cm}^{-2}$  is the saturation dose ( $D_{\text{sat}}$ ). At  $D = D_{\text{sat}}$ , the S surface concentration is no higher than 1–2 at % and the CdS surface is coated with a homogeneous amorphous Cd layer with a thickness of 10–12 Å (Fig. 2).

Having analyzed the spectra shown in Fig. 1, we estimated the main parameters of the energy bands of CdS bombarded by  $\text{Ar}^+$  ions with  $E_0 = 1$  keV at different doses (Table 1). It can be seen that ion bombardment significantly changes the band parameters. At average doses, the narrow acceptor and donor levels form due to the formation of various defects in the band gap near  $E_v$  and  $E_c$  (the bottom of the conduction band); consequently, the average  $E_g$  value for the film decreases. At high doses, the surface layers are metallized (Fig. 2) and the  $E_g$  value decreases almost to zero. Heating of the system to  $T = 900$  K led to the complete evaporation (within the Auger electron spectroscopy sensitivity) of S atoms from the surface, an increase in the concentration  $C_{\text{Cd}}$  to 100 at %, and partial crystallization of the Cd films (insets in Fig. 2). A thin ( $\sim 15$ –



**Fig. 2.** Profiles of the distribution of Cd atoms over the depth  $d$  of the CdS film after bombardment by  $\text{Ar}^+$  ions with energy of  $E_0 = 1$  keV at  $D = 5 \times 10^{16} \text{ cm}^{-2}$  (1) before and (2) after heating at  $T = 900$  K for 30 min. Inset: high-energy electron diffraction patterns (1') before and (2') after heating.

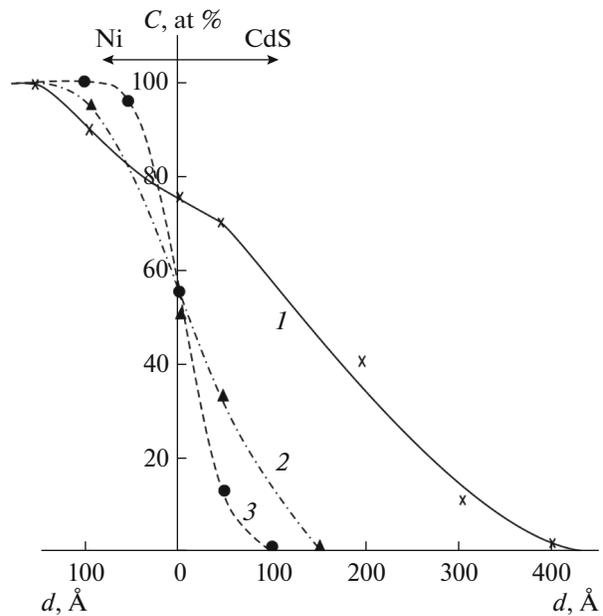
20 Å) transition layer forms between the Cd and CdS films, in which the Cd concentration decreases from 98–100 to ~50 at % (Fig. 2).

At high irradiation doses, an oxide layer forms neither on the surface nor at the Cd–CdS interface. This is due, first of all, to the fact that under ion bombardment the surface layers are effectively purified, in particular, of oxygen atoms. The Schottky-barrier height at the Cd–CdS interface was ~0.4 eV.

In the case of ion energy growth to  $E_0 = 3$  keV, the Cd-film thickness increased by merely 3–4 Å, which is, probably, due to an increase in the Cd-film sputtering intensity with increasing ion energy. At low energies of  $\text{Ar}^+$  ions ( $E_0 = 0.5$ – $0.8$  keV), the Cd-film thickness is no higher than 5–6 Å; in these layers, the sulfur concentration increases to 3–5 at %. We can assume that the optimal energy for forming a pure Cd/CdS film is  $E_0 = 1$ –2 keV.

One of the main problems of microelectronics, especially in large-scale and very-large scale integrated circuits, is the formation of reliable contacts. The requirements for contacts (contacting material) formed on a submicron-layer surface are stricter than for the contacts to thick films. These requirements become much stricter in the case of contacts for microwave devices. One of the main requirements is a small metal–semiconductor transition-layer thickness ( $d \leq 100$ – $150$  Å). The depth of diffusion of the contacting metal ions into the semiconductor is decreased by the formation of a barrier layer on the semiconductor surface.

Further investigations showed that the formation of a Cd film on a CdS surface leads to a sharp decrease in



**Fig. 3.** Distribution of the concentration  $C_{\text{Ni}}$  in the Ni–CdS contacting layer over the CdS-film depth ( $d$ ) for a pure film, (2) after bombardment by  $\text{Ar}^+$  ions with the energy  $E_0 = 1$  keV at  $D = 6 \times 10^{16} \text{ cm}^{-2}$ , and (3) after annealing of the ion-bombarded sample at  $T = 900$  K for 30 min. The nickel-film thickness is ~1000 Å.

the depth of penetration of contacting metal atoms into CdS and creates the conditions for obtaining nanoscale contacts. To do that, a Ni atomic layer with a thickness of ~1000 Å was deposited onto the surface of the investigated CdS films in high vacuum. Figure 3 shows the Ni depth distribution profile for the pure and bombarded by ions CdS films. It can be seen that, in the pure film, the Ni penetration depth reaches 400–500 Å. After ion bombardment, it decreases by a factor of three–four. Post-implantation annealing at  $T = 900$  K leads to a noticeable increase in the Ni diffusion depth as compared with the initial sample. In this case, however, the Ni penetration depth is no larger than 150–

**Table 1.** Parameters of energy bands of the CdS surface after bombardment by  $\text{Ar}^+$  ions with energy of  $E_0 = 1$  keV at different doses  $D$

band parameters	$D, 10^{15} \text{ cm}^{-2}$			
	0	0.50	5.0	50
$\Phi$ , eV	6.35	5.9	5.0	4.3
$E_g$ , eV	2.45	2.4	1.5	0
$\varphi$ , eV	4.2	—	3.7	4.3
$\chi$ , eV	3.9	3.5	3.5	4.3

$\Phi$  is the photoelectric work function corresponding to the top of the valence band  $E_v$  relative to the vacuum level,  $E_g$  is the band gap,  $\varphi$  is the thermionic work function corresponding to the Fermi level  $E_F$ , and  $\chi$  is the electron affinity.

200 Å. The resistivity of the contacting layer in the Ni–CdS and Ni–Cd–CdS systems was no more than 1  $\mu\Omega$  cm. The bulk resistivity of the metal–CdS system remains almost unchanged and lies between  $\sim 5 \times 10^6 \Omega$  cm.

### CONCLUSIONS

Cd–CdS nanofilms with a narrow transition layer were synthesized by bombardment by  $\text{Ar}^+$  ions with a low energy ( $E_0 \leq 3$  keV) and a high dose ( $D \leq 5 \times 10^{16} \text{ cm}^{-2}$ ). It was established that, at low ion doses ( $D \leq 5 \times 10^{15} \text{ cm}^{-2}$ ), the surface is enriched with S atoms and, at high doses, with Cd atoms. These changes lead to a change in the density of states of valence electrons and parameters of the energy bands. In particular, at all ion-bombardment stages, the  $E_g$  value steadily decreases and, at high ion doses, approaches zero. It was shown that the presence of Cd on the surface of CdS facilitates a sharp decrease in the depth of penetration of contacting metal atoms into the CdS film and obtaining reliable ohmic contacts.

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