The Influence Of Argon Ions On The Photoelectric Properties Of A Heterostructure Based On CdTe-SiO_2-Si

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ABSTRACT

This study investigates the effects of argon ion bombardment on the photoelectric properties of a CdTe-SiO_2-Si heterostructure. The research focuses on understanding the mechanisms of photo-electromotive force (photo-EMF) generation in cadmium telluride (CdTe) films, especially the inversion of photo-EMF polarity depending on the wavelength of the incident light. Films deposited at substrate temperatures between 250°C and 300°C demonstrated varying photovoltaic properties across different depths, which were influenced by the deposition angle and film thickness. Through spectral analysis, the study identified three types of samples based on their photo-EMF polarity behavior. The first type consistently showed A-polarity, the second exhibited B-polarity, and the third type displayed polarity inversion depending on the wavelength and illumination direction. Ion bombardment further modified the films' characteristics by reducing thickness and altering conductivity, leading to significant changes in their photovoltaic behavior. The results suggest that the photo-EMF generation mechanisms are depth-dependent, with different regions of the film contributing to the overall photovoltaic response. These findings provide valuable insights into the layer-by-layer localization of photo-EMF generation mechanisms in CdTe films and demonstrate the potential of ion bombardment as a method to tune the photovoltaic properties of semiconductor heterostructures.

Keywords: photoconductivity, short circuit current, ion bombardment, photovoltage, spectral characteristics, photovoltaic effect

1. Introduction

One of the important issues that has attracted particular attention from researchers in the field of solid-state electronics over the past five decades is the mechanism of photo-EMF generation during illumination of crystalline or film semiconductor structures[1]. The most important characteristic of photoelectromotive force is undoubtedly its polarity, since it is determined by the mechanism of separation of nonequilibrium charge carriers, i.e., it is directly related to the nature of this phenomenon. Clarification of the latter is a very important task both in theoretical and practical terms. This is especially true for high-voltage photo-EMF, the nature of which cannot be considered finally established, although efforts in this direction have been made for almost fifty years. The most intensive studies of high-voltage photo-electromotive force (photo-EMF) in cadmium telluride (CdTe) materials commenced in 1958, following the report by Pensak and Goldstein on a pronounced photovoltaic effect in CdTe thin films. They observed voltage values exceeding 100 V per centimeter of film length. This foundational research has since been expanded by subsequent developments, including the use of

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adaptive photo-EMF detectors based on CdTe and its solid solutions, as explored in more recent studies [2,3]. Despite the fact that high-voltage photo-EMF was subsequently discovered on many other substances, cadmium telluride remains one of the main objects of study of the photovoltaic properties of semiconductors. This was largely facilitated by the fact that, according to theoretical studies, cadmium telluride is considered one of the most promising substances for the creation of solar cells.

2. Experimental methodology

One of the most interesting features of the high-voltage photo-EMF in cadmium telluride films is the inversion of its polarity, which occurs when the wavelength of the exciting light changes. Such an inversion on cadmium telluride was first described in [4,5], and was subsequently noted in a number of other works [6,7], for example. The authors of these works note a number of different physical factors in the manufacture of photosensitive samples that affect the type of spectral characteristics of the photo-EMF of these samples. These include: the angle of inclination of the molecular beam to the substrate, the temperature of the substrate, the composition of the vapor in the molecular beam, etc. The most general requirement for the deposition conditions, under which the spectral inversion of the photo-EMF polarity is observed, turned out to be the orientation of the molecular beam at an angle of at least 250 relative to the normal to the substrate. In addition, the inversion of the polarity of the photo-EMF of cadmium telluride films was also observed depending on their thickness or illumination angle. The fact that photo-EMF of different polarity is observed on the same film indicates the action of several, at least two, competing generation mechanisms[8]. In each specific condition, for example, when illuminated by light of a certain region of the spectrum, one of the photo-EMF generation mechanisms dominates, determining its polarity. In the case of simultaneous counter action of two or more charge carrier separation mechanisms, the resulting photo-EMF can be very small or even equal to zero. If we also take into account that in some cases the photo-EMF changes not only in magnitude but also in polarity depending on the direction of illumination (from the film side or from the substrate side), then it is natural to assume that different generation mechanisms are localized in different depth areas of the photovoltaic film: near-surface, bulk and near-substrate. In this case, due to the non-uniform absorption of light (especially short-wave) by the film along the direction of illumination, it is possible to probe the photovoltaic activity of film regions of different depths by illuminating it with light of different wavelengths, from the front and from the rear. In other words, the basic information on the possible layer-by-layer localization of photo-EMF generation mechanisms in films should be contained in the spectral characteristics of the photo-EMF[2,3]. Taking this into account, we attempted to experimentally confirm the layer-by-layer localization of sensitive regions of cadmium telluride films obtained with a fairly wide variation of their preparation modes, providing various photovoltaic properties. To change the ratios of the contributions of the surface and bulk regions of the film, ion bombardment was undertaken, which, along with possible changes in other properties, leads to a decrease in the film thickness. After ion bombardment, the spectral characteristics of the photo-EMF were recorded and compared with the original ones, i.e. those recorded before the bombardment. After implantation of argon ions into films deposited on a SiO_2 –Si substrate, the short-circuit current (Isc) exhibits a decrease across the entire spectral range. This behavior is likely attributable to the destruction of potential barriers and a modification of their asymmetry at the film surface. Such effects may result from the formation of radiation-induced defects, which effectively shunt the barriers responsible for photo-EMF generation, thereby diminishing the overall photoresponse. Additionally, the surface asymmetry is altered, reducing photo-EMF particularly under surface excitation. A twofold reduction in Isc can be associated with the formation of an intermediate layer characterized by a specific resistivity of 10^5 Ω·cm and a thickness of $d = 0.2$ μm, which is consistent with mechanisms observed in other SiO_2 -coated CdTe-based structures[9].

During ion implantation, the diffusion coefficient can increase significantly . Accelerated diffusion is due to the fact that the equilibrium values of the concentration of vacancies and interstitial atoms increase. Accordingly, the diffusion coefficients for vacancies and interstitials increase[10]. It should be noted that the connection of implanted atoms in semiconductors with structural defects of the lattice is often so strong that it slows down the transition of the system to the initial position even in the case of strong diffusion. For this reason, there may be a decrease in photo-EMF during intrinsic excitation. Heating of non-implanted layers under the same conditions does not affect the shape of the Isc spectra in the impurity absorption region, but only increases its value in the intrinsic region by 1.4 times, and FP decreases it by 1.6 times over the entire spectrum, i.e. heating improves the barriers, and the impurity spectrum in non-implanted layers remains unchanged.

As noted earlier, cadmium telluride films were specially doped with silver, which rapidly diffuses into CdTe and can create deep levels with activation energy Ev-0.35 eV . Due to the migration of silver atoms along the intercrystallite boundaries (this is energetically preferable) into the depth of the film, surface acceptor-type centers Ec-1.15 eV are formed along the crystallite boundaries[11,12]. The change in the charge states of such levels leads to an additional change in the barrier height in the region of band bending and the formation of similar potential barriers in the film depth. During implantation, the concentration of tellurium inclusions increased, and copper and silver atoms could getter with these inclusions, and heat treatment promoted the reverse diffusion of these atoms in the region of potential barriers in , the release of copper atoms from tellurium inclusions was observed at 1000C. During ion implantation, these complexes can be destroyed and formed again during heat treatment. The defects created during heat treatment become mobile. They migrate to traps (surfaces, grain boundaries), recombine with each other (for example, an interstitial atom recombines with a vacancy), or form new defects, combining with each other or with defects of a different type (or impurities)[13].

It should be noted that the observed deep levels of 0.4; 0.7 eV in CdTe:Ag on a SiO_2 –Si substrate are apparently associated with the specificity of the formation of crystallite nuclei on SiO_2, and these centers are located predominantly on the side of the barrier where the carrier lifetime is shorter, as indicated by the opposite sign of the photo-EMF during excitation from levels compared to band-to-band generation.

3. Results and discussion

The cadmium telluride films under study were prepared by thermal spraying, which was performed in the working volume of the VUP-4 universal vacuum post at a residual gas pressure of about 10-5 Torr. The cadmium telluride powder was evaporated from a quartz crucible heated by a tungsten coil. The copper plate table on which the substrates were placed was located at a distance of 23 cm from the evaporator and could be heated by a tungsten coil mounted in it to 600°C. In addition, it could rotate around a horizontal axis so that the spraying angle α, i.e. the angle between the normal to the substrate and the direction of the molecular beam, could vary within the range from 15° to 75°. Fused quartz and oxidized silicon plates were used as substrates. The deposition time was automatically regulated by a special shutter located between the deposition table and the evaporator. To record the spectral characteristics of the photo-EMF, an infrared spectrophotometer IKS-14 was used. Sufficient intensity of monochromatic light was provided by choosing a powerful light source (Globar) with an input and output slit of 2 mm. Focused monochromatic light fell on the sample located in oxidized silicon SiO_2 - Si behind a shielded device[9]. The signal from the sample was fed to an electrometric amplifier UI-7 with an input resistance of 100 Ohm and recorded by a recorder ED05-M. Since the resistance of the samples usually exceeds the input resistance of the amplifier by 2-3 orders of magnitude, the measurements are carried out in the short-circuit current mode. In this case, the dependence of the short-circuit current on the light intensity is linear, and when plotting the spectral curves, the signal value was reduced to the same intensity of the incident light.

The samples were bombarded with argon ions in a specialized glass chamber designed for controlled ion treatment. Each sample was mounted onto molybdenum holders connected to a grounded platform, which could be rotated to allow precise orientation with respect to the incident light beam from the monochromator. This setup enabled the irradiation of both the front and back surfaces of the sample under identical conditions. Such experimental approaches are consistent with previous investigations[14,15] on the electrical and dielectric behavior of polycrystalline PbTe films with altered stoichiometry under external influences[14]. An aluminum disk with a diameter of 25 mm served as the anode of the discharge tube, and a molybdenum wire ring located near the sample served as the cathode. To obtain argon ions, the device was subjected to double pumping with a zeolite pump and washing with argon, after which a voltage of 1 ÷ 3 kV was applied between the anode and cathode at an argon pressure of 10^{-1} Torr. The discharge current was 1 ÷ 4 µA. The sample bombardment time varied from 5 to 30 min.

The spectral distribution of short-circuit current (SCC) was studied on 70 cadmium telluride films deposited on SiO2-Si plates. The samples were illuminated both from the film side (front) and from the substrate side (rear) at a right angle. Based on the type of spectral characteristics obtained, the studied samples could be divided into three groups. The main criteria for such a division were the polarity of the photo-EMF and the presence or absence of its inversion depending on the wavelength. In this case, samples with a photo-EMF polarity, when there was a minus at the end remote from the evaporator during illumination, were conventionally called type A samples (or with A-polarity), and those with reverse polarity were called type B samples. The first group consists of samples on which photo-EMF with A-polarity is observed in the entire spectral range both when illuminated from the front and when illuminated from the rear. The second group includes samples that exhibit B-polarity photo-EMF under the same conditions. The third group includes samples that exhibit photo-EMF polarity inversion depending on the wavelength or direction of incident light[16].

Photo-EMF polarity inversion depending on the wavelength was observed in cadmium telluride films deposited at a substrate temperature of Tp = 250°-300°C and deposition angles of α = 30° + 75°. When illuminated with white light, such samples exhibit a resulting effect, since the mechanisms that determine A- and B-polarity partially (or completely) compensate each other in different spectral ranges. The predominance of one of these components determines the polarity of the photo-EMF of the sample. A number of samples exhibited complete compensation of these components: photo-EMF was observed in monochromatic light and was not observed in white light.

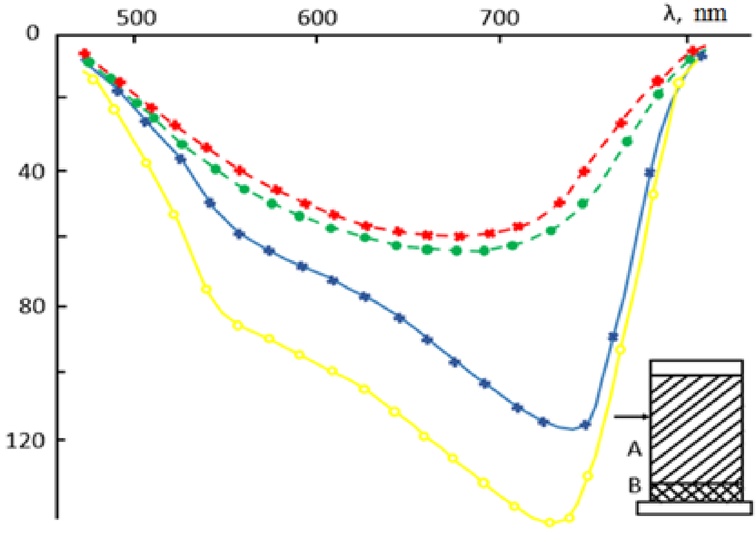

Fig. 1. Typical view of spectral curves for samples of group I.
Designations: yellow line-frontal illumination before bombing, green line-frontal lighting after bombardment, blue line-rear about reduction to bombing, red line-backlighting after argon ion bombardment

The fact that the samples of the third group show a change in the photo-EMF polarity depending on the spectral composition or direction of the incident light (from the film or from the substrate) may indicate the presence of several (at least two) competing generation mechanisms that may be associated with individual film sections located at different depths. One generation mechanism may be localized in the near-surface layer, which absorbs mainly light from the short-wave region of the spectrum, another in the substrate layer, and a third one, associated with the sample volume, between them. In addition, a ballast region may exist in the film volume, i.e. an inactive region in terms of photovoltaics, which can only indirectly affect the photo-EMF generation conditions by shunting the active part and also being an absorbing medium[8]. Using such a model representation, it is possible to mainly explain the course of the spectral dependence of the SCC observed in samples of all three groups, when illuminated from the front and from the rear. Examples of such dependence of the TSC on some samples from different groups are shown in Fig. 1-5 by solid curves, where the supposed layer-by-layer structure of the studied films is also shown schematically based on the model concepts stated above. In these diagrams, the shaded areas correspond to photovoltaically sensitive interlayers with certain mechanisms of photo-EMF generation (A or B), and the unshaded areas correspond to ballast interlayers. The sizes of these areas conventionally characterize the degree of photovoltaic activity of the sensitive interlayers and the absorption capacity of the ballast interlayers (i.e., they do not reflect the actual thickness of the interlayers). Let us follow the course of the spectral dependence of the TSC shown in these figures. For samples of group I, a typical course of such a dependence is shown in Fig. 1. It can be explained if we assume the simultaneous coexistence of A- and B-mechanisms in these samples, with the B-mechanism being localized in the subsurface region. In this case, illumination of the sample from below activates the B-mechanism, which partially compensates for the contribution of the A-mechanism. Thus, for samples of group I, the A-mechanism is the main one in generating photo-EMF.

The course of the spectral characteristics taken from the samples of group P, an example of which is shown in Fig. 2, can be explained in a similar way, only here the main mechanism for generating photo-EMF will be the B-mechanism, localized in the volume and in the subsurface region.

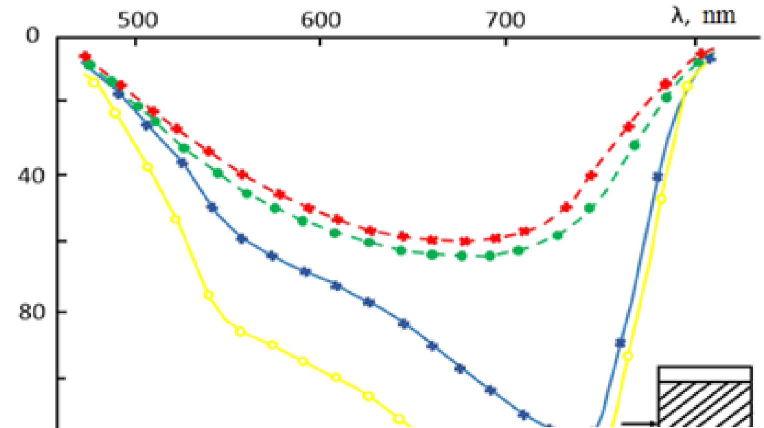

Fig. 2 Typical view of s
Designations: yellow
lighting after bombardment, blu
after argon ion bombardment

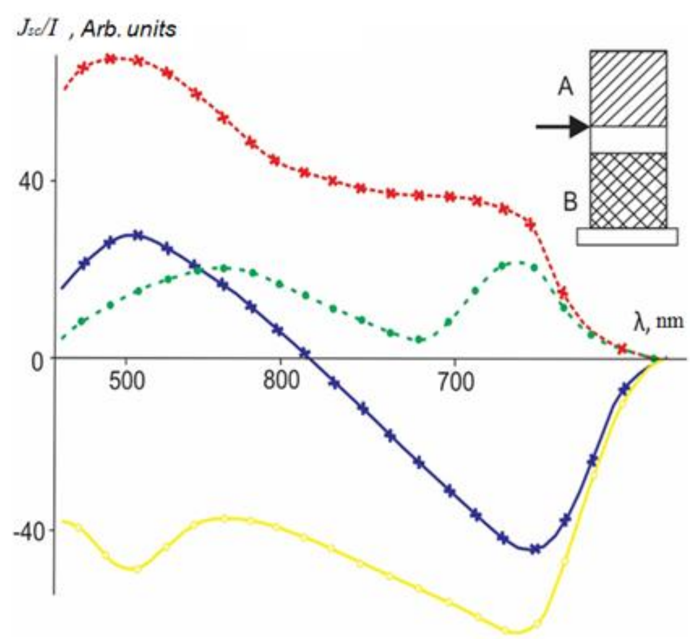

Fig. 3 Typical view of spectral curves for samples of group III. /N° II, 52/.
Designations: yellow line- frontal illumination before bombing, green line- frontal lighting after bombardment, blue line-rear about reduction to bombing, red line- backlighting after argon ion bombardment

Examples of different behavior of the spectral dependence of the TCD for samples of group III are shown in Figs. 3-5. The behavior of the curves in these figures indicates that in this case different spectral regions correspond to the determining role of different mechanisms, A or B, i.e. the generation mechanisms themselves are localized at different depths, as shown schematically in the figures next to the curves. To verify the correctness of this assumption, the films under study were subjected to ion bombardment, which resulted in a change in their thickness due to etching from above. In all the figures given, the assumed depth of ion etching is shown by a horizontal arrow on the left of each diagram. The behavior of the spectral curves taken after ion bombardment is shown in Fig. 1-5 by dashed lines. The direction of change in these curves as a result of horse bombardment generally fits satisfactorily into the framework of the expressed ideas, if we consider that bombardment mainly

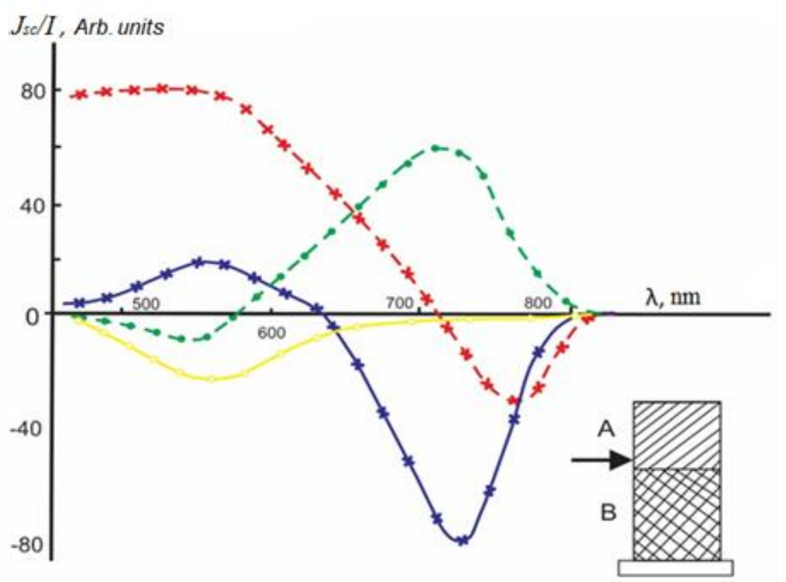

Fig. 4 Typical view of spectral curves for samples of group III. / N° 24 ,27, 36, 38/.

Designations: yellow line- frontal illumination before bombing, green line- frontal lighting after bombardment, blue line- rear about reduction to bombing, red line- backlighting after argon ion bombardment

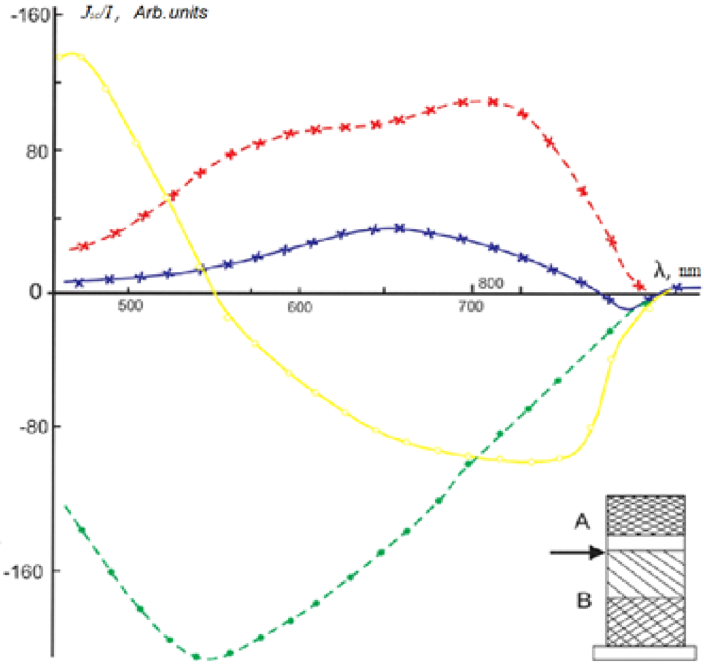

Fig. 5 Typical view of spectral curves for samples of group III. / N° 25 ,42, 54, 55/.

leads to layer-by-layer etching of the film.

4. Conclusions

In conclusion, Naturally, in the form as it is presented in Fig. 1-5, the schemes of the layered structure of the films do not contain sufficient information to obtain quantitative data on the course of the spectral curves on their basis, but they mainly reflect the qualitative side correctly. For example, the results shown in Fig. 5, based on such positions, can be perceived with some stretch. Apparently, this is due to the fact that ion bombardment leads not only to a decrease in the film thickness, but also causes other changes in it, for example, a change in conductivity, which, in turn, will quantitatively affect the photovoltaic properties of the film. Thus, the spectral characteristics of the photo-electromotive force (photo-EMF) in cadmium telluride (CdTe) films can serve as an informative indicator of the uniformity or non-uniformity of their photovoltaic properties throughout the film thickness—from the surface down to the substrate. Variations in photovoltaic behavior in near-surface regions are often linked to localized deformation of the condensate crystal lattice (either expansion or compression), which arises from differing film growth conditions. Specifically, tensile deformation is known to enhance not only the micro-potential barriers but also their asymmetry at crystallite boundaries, thereby facilitating the generation of photo-EMF. These effects are in agreement with recent studies that examine quantum-dimensional near-surface recombination in CdTe microstructures[17], as well as the diffusion dynamics of copper atoms in Pb-doped polycrystalline CdTe films, which influence the local potential landscape and charge transport mechanisms [18].Under compression deformation, they partially go deep into the crystallites, which leads to a decrease in the barrier height and partial removal of their asymmetry. Measurement of the barrier height from deformation depends on the change in the energy spectrum of charge carriers. The results obtained can be used for various specific cases of studying photoelectric phenomena in inhomogeneous semiconductor films.

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