

Si/Zn_xCd_{1-x}Te heterostructures with different Zn contents: growth, electrical and photoelectrical properties

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Abstract. The Zn_xCd_{1-x}Te films with $x = 0 \div 0.97$ are grown by vacuum deposition in quasi-equilibrium conditions on single crystal Si (111) substrates. The details of the growth process were analyzed. The possibilities of the quasi-closed volume method for producing high quality homogeneous layers of solid solutions were evaluated. It is shown that this method is very effective for the production of films with $x < 0.1$ and may be implemented at condensation temperatures up to $\sim 300^\circ\text{C}$. Studies of electrical and photovoltaic properties showed high quality of Zn_xCd_{1-x}Te layers and structures in general. This is, in particular, evidenced by increasing photosensitivity in the region of absorption of the film material, and of the structure as a whole, increasing integral sensitivity with zinc doping, a significant reduction in non-ideality factor in solid solution films as compared with CdTe films. We have established an increase of mechanical stability of the structure with increasing Zn content, expressed in maintaining the strength during repeated thermal cycling. As a result, the manufactured Si/Zn_xCd_{1-x}Te heterostructures can serve as a basis for fabrication of multijunction solar energy converters.

1. Introduction

Monolithic multijunction structures are promising for optoelectronic applications including the creation of the cascade converters of solar energy. Currently, the greatest value of the conversion efficiency of solar energy was received on multijunction structures based on III-V compounds [1]. However, due to a number of technological and economic reasons, the multijunction structures that combine II-VI compounds with silicon are serious competition for the structures based on III-V compounds [2,3]. Among the possible combinations with silicon, of increased interest is a combination of silicon and cadmium telluride - a compound with an optimal set of physical parameters for photoelectric conversion of solar radiation [4]. The principal limitation in using heterostructures (HS's) of Si/CdTe is a high ($\sim 14\%$) mismatch of lattice parameters of materials. However, the theoretical analysis shows [3] that this problem can be eliminated if, instead of pure CdTe, the Zn_xCd_{1-x}Te solid solutions are used, for which a misalignment is significantly less.

The main goal of the work was to develop a method of growing crystalline Zn_xCd_{1-x}Te films on Si wafers and to create structures which can be used as a platform for further manufacturing tandem two-junction solar cells. The specific goals of the work were as follows:

- the growth of epitaxial Zn_xCd_{1-x}Te films on single-crystal Si substrates with a sufficiently high crystallinity and a controlled content of zinc;
- study of electrical properties of the Si/Zn_xCd_{1-x}Te structures with different content of Zn in solid solutions in order to characterize the obtained films and structures.



2. Growth experiments

The objects of the study are Si/Zn_xCd_{1-x}Te HS's with an anisotype n-Si/p- Zn_xCd_{1-x}Te heterojunction. The samples are planar HS's consisting of a silicon substrate (a single crystal silicon wafer of <111> orientation) coated by a solid solution film of about 1-2 microns thickness. As contacts to silicon and Zn_xCd_{1-x}Te films, we used In-Ga alloys of compositions close to eutectic and a two-layer coating of Ti(~70 Å)/Al(~1 μm), respectively.

The problem of manufacturing high-quality single-crystal films of cadmium telluride has a long history associated primarily with the development of technology of IR devices based on HgCdTe solid solutions [5]. The obvious advantages of vapor-phase techniques for epitaxial growth of CdTe films have been implemented in the framework of different technological solutions from vacuum deposition, including ultrahigh vacuum conditions [6], to vapor-phase reactions techniques using organometallic compounds [7], in conditions close to equilibrium and far from those [8]. All of these methods in the optimum mode allowed us to obtain epitaxial layers, the crystal quality of which is mainly determined by the degree of purity of the precursors and by the ratio of the lattice parameters of CdTe and the substrate material. In this paper, vacuum deposition in a quasi-closed volume has been selected as a method for the films (structures) preparation. This method allowed, for relatively low cost, to carry out the condensation of films in a wide range of condensation conditions, including vapor, the parameters of which in each isothermal section (in the direction of transfer) are as close as possible to the thermodynamic equilibrium ones (the mode of gas-dynamic flow [9]). Moreover, the method allows to obtain uniform films of large area.

The evaporation chamber is a split graphite cylinder, the bottom of which is tightly joined with a graphite block with the evaporated substance (CdTe charge). An upper graphite cover, tightly closing the cylinder, is also a substrate holder. The calculations performed by the method [9] have allowed to design an evaporation chamber, in which the condensation is possible in both a laminar vapor flow (the gas-dynamic mode) and a molecular vapor flow, at temperatures of condensation $T_C = 250\div 400^\circ\text{C}$ in a wide range of values of relative vapor supersaturation (1÷100) at the crystallization surface.

The films were deposited on monocrystalline silicon wafers, previously cleaned from natural oxide using the modified RCA cleaning method [10]. The method included the removal of organic contaminants from the silicon surface, etching in HF, soaking in deionized water with subsequent mild oxidation. Before loading Si substrate into the evaporation chamber, the oxide was removed by soft etching in a dilute HF solution. The final purification step was annealing in vacuum immediately before evaporation. Removal of the oxide is an important procedure because, as pointed out in [11] (and according to our observations), the presence of native oxide on the surface of Si leads to the growth of polycrystalline CdTe films at all substrate temperatures and growth rates.

The composition of the solid solution film was controlled during the manufacturing process by changing the ratio of CdTe and ZnTe in the evaporation source.

According to the method described above, the Si/CdTe heterostructures on Si-substrates with different carrier concentrations were produced. The highest quality films of cadmium telluride have been obtained under quasi-equilibrium conditions with laminar vapor flow and condensation temperatures of ~ 350°C. Analysis of layers morphology showed that they are the textured block structures oriented along the <111> growth direction. The surface is represented by well-faceted crystallites with an average size of more than 1 μm, separated by straight boundaries. The main types of observed structural defects are microtwins and dislocation etch pits. In addition, we observed antiphase domains (evidence of layer-by-layer growth) and micron-sized fragments of hexagonal shape in some samples.

When growing films of Zn_xCd_{1-x}Te solid solutions with a low zinc content (x is of order of a few percent), the growth parameters and morphology of the films practically do not differ from those for the growth of pure cadmium telluride. However, in the experiments on production of solid solution films with $x > 0.1$ it has been found that increasing zinc content in the vapor requires raising the

temperature of the evaporation source (above 650°C), and, as a result, changing the geometric parameters of the evaporation chamber and performing the process in the mode of molecular beams. The condensation temperatures do not exceed 400°C, since at higher temperatures the films crystallize on Si (111) substrates predominantly with a hexagonal structure (wurtzite) [12].

The composition of the solid solution films was determined based on the analysis of the transmission spectra in the fundamental absorption edge region for the films of $Zn_xCd_{1-x}Te$ on glass, with a subsequent determination of the band gap E_g and the calculation of x from the composition dependence $E_g(x)$ [13]:

$$E_g(x) = E_g(\text{ZnTe}) - [E_g(\text{ZnTe}) - E_g(\text{CdTe})] (1 - x) + Bx (1 - x) \quad (1)$$

In the calculation we used: $E_g(\text{ZnTe}) = 2.24$ eV; $E_g(\text{CdTe}) = 1.48$ eV; $B = 0.34$ ($T = 300$ K) [14]. The optical experiments were performed by a Fourier spectrometer Vertex-80x. The light source was a halogen lamp (350-3500 nm).

Considering the fact that:

$$\alpha L = A \frac{\sqrt{h\omega - E_g}}{h\omega}, \quad (2)$$

where α - the absorption coefficient; L - thickness of the film, the value of E_g is determined by the cutoff value on the axis $h\omega$ of the experimental dependences represented in the coordinates $(\alpha L \times h\omega)^2 - h\omega$, for example, for the samples with the lowest ($x = 0.03$) and the highest ($x = 0.97$) concentrations of Zn in solid solutions, presented in figure 1.

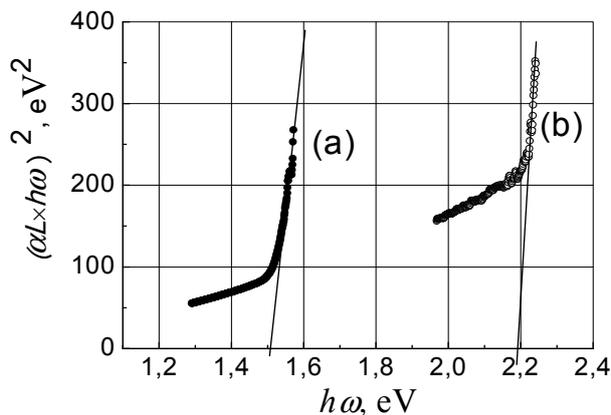


Figure 1. Determination of the band gap of the solid solution films with different Zn contents for the samples with the lowest $x = 0.03$ (a) and the highest $x = 0.97$ (b) concentrations of Zn in $Zn_xCd_{1-x}Te$ films

Thus, $\text{Si}/Zn_x\text{Cd}_{1-x}\text{Te}$ HS's with the Zn content (x) in solid solution films varying from 0 to 0.97 were fabricated. All the films had p-type conductivity. The hole concentration determined from the capacitance-voltage characteristics was $1 \times 10^{13} - 1 \times 10^{15} \text{ cm}^{-3}$. The dependence of the carrier concentration on the Zn content is not found in the present work. The carrier concentrations in n -Si substrates were $5 \times 10^{14} - 1 \times 10^{18} \text{ cm}^{-3}$. The film thickness was 1-2 μm , the size of a structure element for subsequent measurements was $5 \times 5 \text{ mm}^2$.

An important feature of the structure, relevant for subsequent fabrication of two-junction solar energy converters, is the mechanical strength. Indeed, due to a high lattice mismatch between Si and CdTe, as well as a significant divergence between the values of their thermal expansion coefficients, the CdTe layer is in a highly stressed state and can be destroyed by heating resulted from these stresses. At the same time, one of the basic operations during fabrication of multijunction structure components is the formation of a p - n junction in $Zn_xCd_{1-x}Te$ films, which is usually performed by thermal diffusion of impurities from the impurity layer previously deposited on the surface of the wide-gap material. The typical values of the temperature of the diffusion process (for In or Cl) are about 300°C [15]. Therefore, the grown structures must withstand a long-term heating up to these temperatures without destruction. Our experiments show that CdTe films on Si substrates are

destroyed (exfoliate) when heated up to these temperatures. However, with the introduction of Zn into the film the mechanical stresses are reduced. Thermocycling of films containing Zn in the range of 20÷300°C does not result in destruction of films on a substrate. This effect was consistently observed at $x > 0.1$. Thus, the introduction of zinc in CdTe films stabilizes the mechanical properties of the structures.

3. Photoelectrical and electrical experiments

All obtained HS's with an anisotype $n\text{-Si}/p\text{-Zn}_x\text{Cd}_{1-x}\text{Te}$ heterojunction are photosensitive. At low zinc content in films ($x < 0.1$), the integral photosensitivity increases monotonically with increasing x by about an order of magnitude compared with the structures of Si/CdTe (when $x = 0.1$). This fact apparently testifies to improving the quality of the layers with the introduction of zinc, and, consequently, of the heterostructure as a whole. By improving the quality of the layers, in this case, we mean the reduction in growth defects density (stacking faults, low angle boundaries, regions with wurtzite structure) and, mainly, misfit dislocations with decreasing lattice mismatch of HS components. The increase in photosensitivity was observed in the whole spectral range, both in the long-wavelength region (Si) and in the short-wavelength one ($\text{Zn}_x\text{Cd}_{1-x}\text{Te}$) (figure 2(a)).

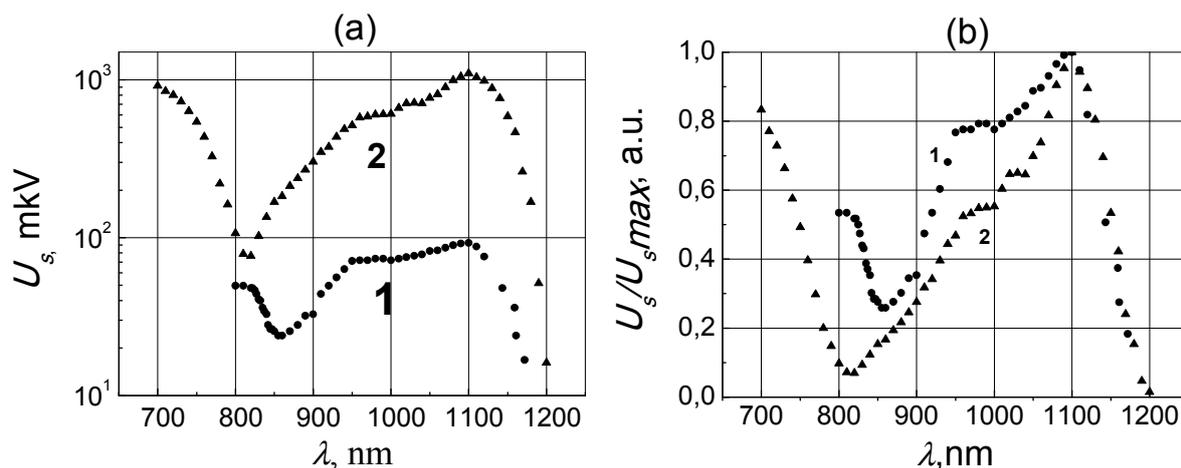


Figure 2. The spectral distribution of the photo-emf (U_s) in Si/CdTe (1) and Si/Zn_{0.1}Cd_{0.9}Te (2) heterostructures. (a) – the absolute value U_s ; (b) – the relative units (U_s/U_{smax})

There are two clearly distinguished regions in the spectral characteristics of HS (figure 2(a)) : a long-wave one (with a red edge at about 1100 nm) corresponding to the absorption of Si and a short-wave one (with a red edge at about 840 nm) corresponding to the absorption of the wide-gap material. With increasing Zn content in the film, the photoresponse red edge for wide bandgap semiconductors is shifted to shorter wavelengths (figure 2(b)). The shift value correlates satisfactorily with the results of the fundamental absorption edge studies. The signs of the photo-emf in both regions were the same (negative, minus at Si). The relation between the photo-emf in the long and short wavelength regions depends on the ratio of the concentration of charge carriers in the base region of the HS. For a low content of Zn ($x < 0.1$) we found a tendency to a relative increase in sensitivity in the short-wave region with increasing x .

The current-voltage characteristics of the $n\text{-Si}/p\text{-Zn}_x\text{Cd}_{1-x}\text{Te}$ HS's are rectifying (figure 3). At low forward bias ($U = 0\text{-}3$ B), the current-voltage characteristics are satisfactorily described by the relation $I \sim \exp(eU/\beta kT)$, where β – the non-ideality factor. The analytical form of the dependence indicates that the conductivity is carried out according to the scheme of thermal emission with significant

recombination in the space charge region. The value of β characterizes the contribution of recombination in the space charge region.

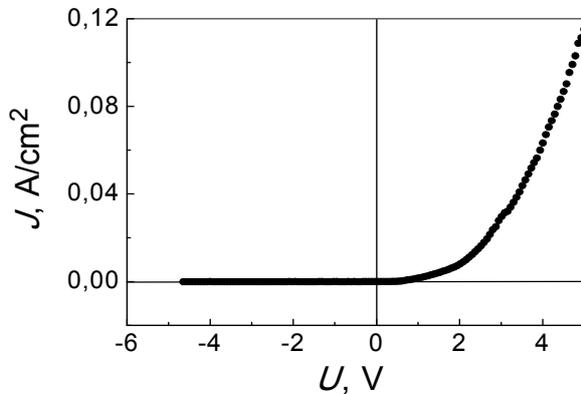


Figure 3. Typical current-voltage characteristic of the $n\text{-Si}/p\text{-Zn}_x\text{Cd}_{1-x}\text{Te HS}$

The main centers of recombination in the space charge of the heterojunction are the states associated with the misfit dislocations. When increasing content of Zn in the film, the mismatch of lattice parameters of Si and the solid solution decreases. As a result, the density of misfit dislocations also decreases, and the contribution of recombination on the boundary states reduces. This is reflected in the decrease in the value of β . This very effect was observed in our study of current-voltage characteristics at low forward bias. For Si/CdTe HS (the greatest mismatch) the experimentally determined β takes a value of 5-7 (figure 4(a)). When we change the film composition by increasing the content of Zn, the value of β decreases and at $x \sim 0.1$ it reaches the minimum value $\beta = 2.1$ (figure 4(b)). With a high content of Zn ($x > 0.5$) the value of β increases. We attribute this effect to the change in the conditions of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ films growth at large values of x , i.e. to the transition from quasi-equilibrium conditions of condensation (small x) to condensation from the molecular flow (large x).

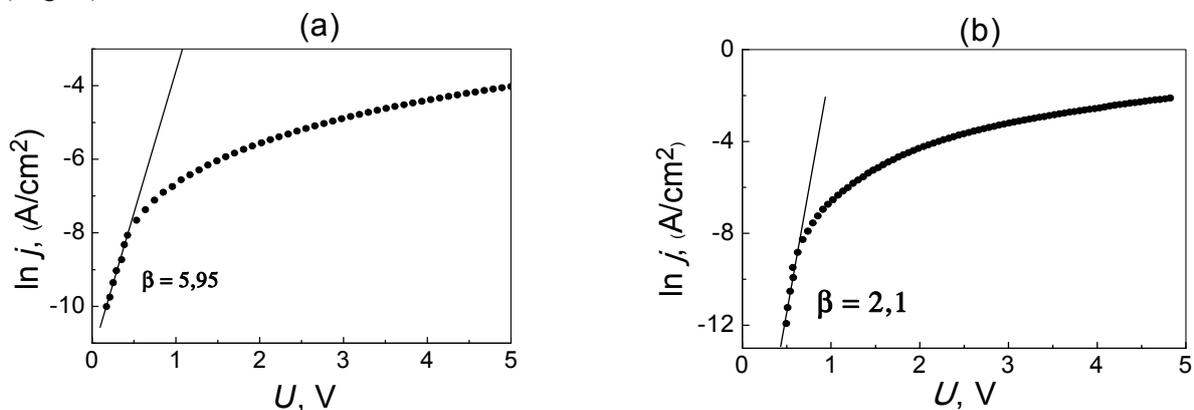


Figure 4. Direct branches of the current-voltage characteristics of the $\text{Zn}_x\text{Cd}_{1-x}\text{Te HS}$'s with different contents of Zn in the film: a) $x = 0$, b) $x = 0.1$

At high forward bias the voltage dependence on the current is described by a law $I \sim U^m$, m usually takes values of $1.5 \div 2.0$. Apparently, this dependence is associated with injection currents in the wide-gap material [16].

4. Results and discussion

As a result of technological experiments, we prepared $\text{Si}/\text{Zn}_x\text{Cd}_{1-x}\text{Te HS}$'s with various zinc content in the films of solid solutions ($x = 0 \div 0.97$). When manufacturing HS's with $x < 0.1$, the growth of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ films can be carried out in the gas-dynamic flow mode (quasi-equilibrium conditions of condensation). The films obtained under such conditions have a uniform thickness over an area of

about 20 cm² and represent large-block texture with a characteristic crystallite size of 1-2 microns. Along with structural uniformity, the films are homogeneous in a number of physical parameters: the variation of the electric and photoelectric parameters of individual elements in different parts of the plate does not exceed a few percent. HS's possess photosensitivity in a wide spectral range (700 – 1100 nm) with the photoresponse signals comparable in the long-wave and short-wave spectral regions. The presence of sensitivity in the absorption region of the solid solution suggests, in particular, the high quality of the film material. With increasing Zn content in the Zn_xCd_{1-x}Te layer we observed increasing in signal in the short-wavelength region and also increasing of the integrated sensitivity of HS. Apparently, this is due to an increase in the structural perfection of the films primarily by reducing the mismatch of the lattice parameters of HS components with increasing x . Obviously, this improves the quality of metallurgical boundaries of HS, decreases the density of misfit dislocations, reduces the contribution of recombination at the boundary states. The analysis of current-voltage characteristics showed a significant reduction in the ideality factor β for the HS with a film of the Zn_xCd_{1-x}Te solid solution, which also confirms a significant improvement in the quality of the boundary.

Decreasing mismatch of lattice parameters of the Si/Zn_xCd_{1-x}Te HS components with increasing Zn content has another important consequence. Reduction of mechanical stress is manifested in the stabilization of mechanical properties of the structure and in the ability not to be destroyed at high temperatures. This allows us to use the thermal diffusion technique to form a p-n junction in the layer of the solid solution.

The films of Zn_xCd_{1-x}Te with a high zinc content ($x > 0.1$) were possible to obtain only in the regime of molecular beams. In this case the uniformity and quality of layers are significantly reduced. This, in particular, is reflected in a significant decrease in the integral photosensitivity of HS. However, when designing a solar energy converter it is desirable to use the solid solutions with the Eg value which does not differ much from the optimal value of 1.5 eV, i.e. the materials with a low content of zinc.

Thus, the Si/Zn_xCd_{1-x}Te HS with a zinc content in the film of the solid solution $x \sim 0.1$, obtained by vacuum deposition in quasi-equilibrium conditions have the necessary quality and mechanical properties and can serve as a basis for further manufacturing two-junction solar energy converters.

5. Conclusion

The main result of this work is the preparation of Zn_xCd_{1-x}Te HS's with different contents of Zn in the film ($x = 0 \div 0.97$). It was found that the technique of deposition in a quasi-closed volume allows to produce uniform layers of the solid solution on the surface with an area of ~ 20 cm². The Zn_xCd_{1-x}Te films make a tight contact with a Si substrate, and are not destroyed during cyclic heating up to 300°C. This quality is manifested only with the introduction of Zn in the film and the structures are stable against destruction even at low zinc content (\sim a few percent). Studies of electrical and photovoltaic properties showed a sufficiently high quality of the layers of Zn_xCd_{1-x}Te and structures as a whole. This is, in particular, confirmed by the photosensitivity of the structures in the region of absorption of the film material and structure as a whole, the increase in the integral sensitivity with the introduction of zinc, a significant decrease of the non-ideality factor of the Zn_xCd_{1-x}Te films compared with CdTe films. As a result, we have manufactured the structures that can serve as a basis for further fabrication of multijunction solar energy converters.

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