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The Synthesis and Investigation of the Electrical Properties of Tricadmium Diarsenide with MnAs Nanogranules

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Abstract—Samples of tricadmium diarsenide with MnAs nanogranules (44.7 mol % MnAs) are synthesized. The morphology of the samples is studied by X-ray phase analysis and electron microscopy. The electrical properties of tricadmium diarsenide with MnAs nanogranules are studied in a range of temperatures of 77–372 K. It is found that the voltammetric characteristics are symmetrical relative to the inversion of the voltage sign at this temperature, and their deviation from ohmicity at a certain threshold voltage and decrease in the region of ohmicity with the growth in temperature are determined by the increase in the breakdown probability in a field above 5×10^4 V/m.

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INTRODUCTION

The investigation of magnetic and semiconducting properties in one material is of interest both in terms of the development of spintronics and for fundamental research. The fundamental interest in the investigation of magnetic semiconductors is determined by the fact that magnetic and exchange interactions play a substantial role in them. The interest in the investigations of a narrow-gap semiconductor, tricadmium diarsenide, is determined by the results of the theoretical [1] and experimental [2] works, in which the belonging of cadmium arsenide to bulk Dirac semimetals is justified. Tricadmium diarsenide has an advantage over other bulk Dirac semimetals known to us, BiO_2 and Na_3Bi [3, 4], thus, it is stable and demonstrates high mobility of charge carriers (9×10^6 cm^2 V^{-1} s^{-1} at 5 K) which exceeds the mobility of the charge carriers in graphene [5].

The charge carriers in tricadmium diarsenide are distinguished by a low effective mass and a high mobility. The question of the zone structure of the tricadmium diarsenide narrow-gap semiconductor has been studied for quite a long time, and zone inversion is proposed in some works along with the zero-gap state [6]. The zone evolution in ternary and quaternary solid solutions based on cadmium arsenide is of interest as an individual task.

Manganese is dissolved in tricadmium diarsenide to form a wide region of ternary solid solutions $(Cd_{1-x}Mn_x)_3As_2$. The exceedance of the concentration of manganese leads to the formation of a composite based on tricadmium diarsenide which contains inclusions of manganese arsenide along with the solid solution $(Cd_{1-x}Mn_x)_3As_2$. The ferromagnetic phase of manganese arsenide crystallizes in a hexagonal lattice $P63/mmc$ with the unit cell parameters $a = 3.72$ Å and $c = 5.71$ Å. A transition from a hexagonal structure of the type of NiAs with the $P63/mmc$ symmetry to an orthorhombic structure of the type of MnP with the *Pnma* symmetry was observed in MnAs at room temperature with the increase in pressure; the transition occurs at pressure $P_{tr} = 0.45$ GPa [7].

A compound MnAs possesses ferromagnetism with the Curie point slightly above room temperature (318 K), which makes it a promising material for use in various elements of spintronics which function in the terahertz region [8–10].

The aim of this work is to synthesize a composite of tricadmium diarsenide with MnAs nanogranules and investigation of the mechanism of violation of Ohm's

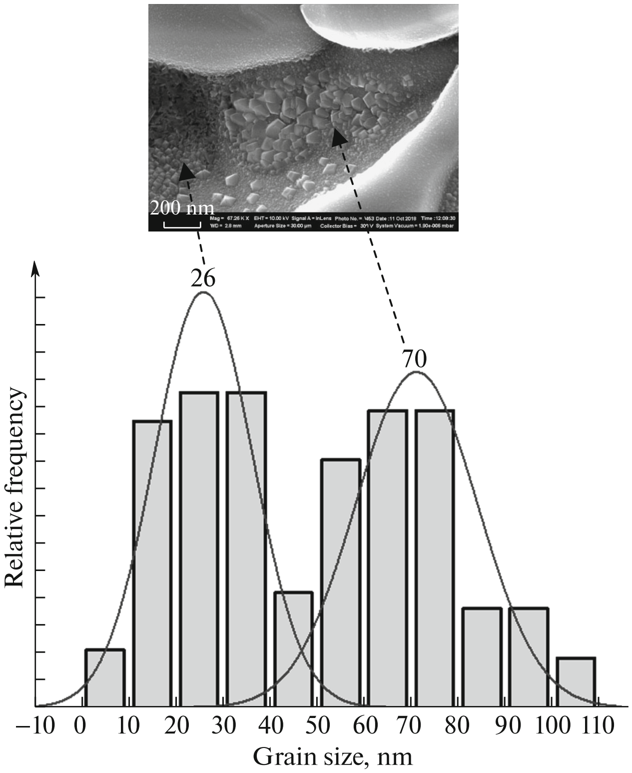

Fig. 1. Size distribution of the MnAs nanoclusters in a Cd_3As_2 + 44.7 mol % MnAs composite obtained using a Merlin scanning electron microscope (Carl Zeiss).

law by measuring the voltammetric characteristics (VACs) in a range of temperatures of 77–372 K.

MATERIALS AND METHODS

Synthesis

The synthesis of the alloys of tricadmium diarsenide with MnAs nanogranules was performed by alloying the initial powders of tricadmium diarsenide with manganese according to the reaction $3CdAs_2$ + 4Mn → Cd_3As_2 + 4MnAs. The bulk samples of Cd_3As_2–MnAs were synthesized by the vacuum ampoule method from individual elements in graphitized evacuated ampoules in an electric oven with automated temperature control with an accuracy of up to 1 K [11]. To decrease the effect of transfer of the volatile component, arsenic, to the free volume of the ampoule, the ampoule was placed into the isothermal zone of the oven. The synthesis occurred in several stages. Melting of cadmium occurred during the first stage with the duration of 2 h. The interaction of the cadmium melt and finely dispersed manganese with gaseous arsenic occurred during the second stage with the duration of 48 h. The interaction of the melt of Cd_3As_2 with MnAs and their subsequent homogenization occurred during the third stage with the duration of 96 h. The quenching of the sample in a room-temperature aqueous medium was performed during the fourth stage at a rate of 13 K/s.

Procedure for Measuring VACs in a Range of Temperatures of 77–372 K

The VACs were measured in a range of temperatures of 77–372 K. When measuring the temperature dependences of the VACs, a sample with contacts was placed into an air-tight chamber filled with gaseous helium under atmospheric pressure, which was at first immersed into a liquid nitrogen vessel for the measurements in a range of temperatures of 77–300 K and then was placed into a thermostat for the measurements in a range of temperatures of 300–372 K. The electromotive force on the sample and readings of the copper–constantan thermocouples were measured using a Shch300 potentiometer. When measuring the VACs depending on temperature, the voltage and current were recorded using a Keithley 2000 millivoltmeter.

RESULTS AND DISCUSSION

Tricadmium diarsenide with nanogranules containing 44.7 mol % MnAs is a complex system consisting of ferromagnetic MnAs granules randomly arranged in a Cd_3As_2 semiconducting matrix. Such a morphology determines the nonuniform distribution of the electric field in the bulk of the sample. The electron microscopic studies performed using a Merlin field-emission scanning electron microscope (FE-SEM) (Carl Zeiss) confirmed the presence of MnAs nanoparticles with the characteristic diameters from 10 to 50 nm inside the tricadmium diarsenide matrix (Fig. 1). As is seen from the figure, the characteristic diameters of the MnAs nanoclusters predominantly are 20–30 nm. In our opinion, individual specimens with sizes over 50 nm can only be present in the near-surface regions rather than in the bulk of the composite because this would have led to a substantial increase in the energies of deformation of both the matrix and its inclusions. Thus, it can be quite reasonably considered that the bulk physical properties of the Cd_3As_2 + 44.7 mol % MnAs composite material that we have studied are determined by MnAs nanoclusters with diameters from 20 to 30 nm. The X-ray diffraction pattern of the Cd_3As_2 + 44.7 mol % MnAs nanocomposite (Fig. 2) confirms that it consists of two phases, namely, tricadmium diarsenide and manganese arsenide. The microstructure of the sample evidences that there has been eutectic separation of the melt into a system consisting of two substances, namely, tricadmium diarsenide and manganese arsenide, upon solidification. A distinguishing feature of the system of tricadmium diarsenide with MnAs nanogranules is the presence of a significant region of immiscibility of the melts of tricadmium diarsenide and manganese arsenide, which also affects the struc-

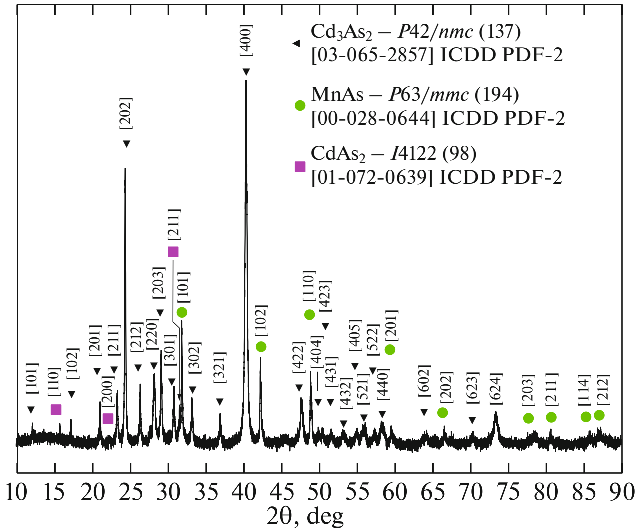

Fig. 2. X-ray diffraction pattern of a sample of Cd_3As_2 + 44.7 mol % MnAs.

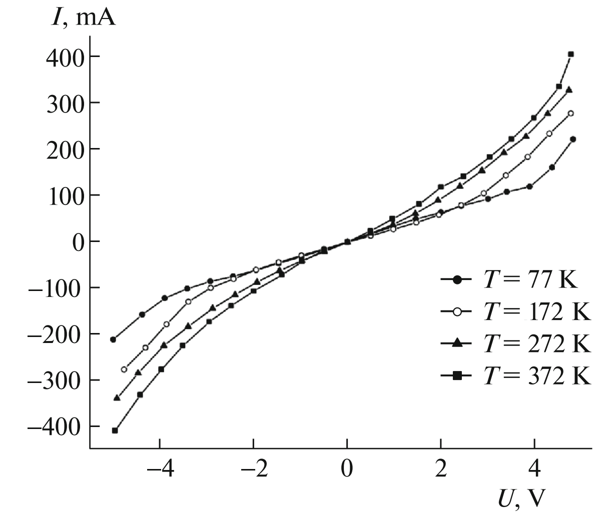

Fig. 3. Temperature dependence of the VACs of a Cd_3As_2 + 44.7 mol % MnAs composite.

ture of the alloy. Such an almost uniform arrangement of the ferromagnetic nanospheres with almost the same diameters in the nonmagnetic matrix is a process advantage in the production of magnetic data carriers from them because the ordered arrangement of the magnetic particles in the matrix occurs naturally.

The VACs of a sample of the Cd_3As_2 + 44.7 mol % MnAs composite with the dimensions 4 × 2 × 1.5 mm measured in two directions of the applied voltage in a range of temperatures of 77–372 K are presented in Fig. 3. The characteristics are symmetrical at both current directions. The following sections of the VACs can be clearly distinguished, e.g., for 272 K: 1, a region at weak electric fields $U = 2$ V ($E < 5 \times 10^4$ V/m), where there is a linear growth in the current on voltage that corresponds to the ohmic region, and 2, a region at higher fields ($E > 5 \times 10^4$ V/m), where the VAC deviates from ohmicity, in which deviation of the current from the linear growth is observed. As is seen from the figure, the maximum value of the current is symmetrically changed with temperature upon changing the direction of the applied voltage: at $U = -5$ V, the current grows from –200 to –400 mA, while at $U = 5$ V it grows from 200 to 400 mA with the growth in temperature. The curves of dependence $I(U)$ are qualitatively similar to each other, but nonlinearity manifests at higher voltages and has a sharper character at the liquid nitrogen temperature. It is seen from the figure that the VAC corresponds to a situation in the case of which the current flows by a metal–semiconductor scheme and manifests dependences characteristic for the structures with a barrier in the region of contact of the metal (MnAs) and the semiconductor (the layer of the tricadmium diarsenide matrix) [12].

It is known that, in the case of a strong decrease in the barrier height, the concentration of the minority charge carriers increases by the exponential law $N = N_0e^{rt}$ (where N is the number of the minority charge carriers, r is the coefficient of proportionality, and t is the time during which the barrier height is changed) with the growth in the voltage, and field emission takes place [12], which is particularly what is observed in the experiment in the region of violation of the Ohm's law.

This is explained by the fact that the electrons in the semiconducting layer of tricadmium diarsenide near the barrier are excited to higher energy levels with the growth in temperature and, hence, the probability of the tunnel passage through the barrier increases with the growth in the voltage.

It is seen from Fig. 3 that the voltage at which the linear ohmic growth in the current is violated decreases with the growth in temperature (77 K, 4 V; 172 K, ~2.5 V; 272 K, ~2 V; 372 K, ~1.5 V). The observed negative temperature coefficient of the dependence of the value of the voltage at which the linear growth in the current on voltage is violated is characteristic of the case of thermal breakdown as opposed to the avalanche breakdown that takes place in the case of a positive temperature coefficient.

CONCLUSIONS

The experimental study of a Cd_3As_2 + 44.7 mol % MnAs composite in a range of temperatures of 77–372 K has shown that the VACs are symmetrical in the case of a change in the sign of the voltage being applied at this temperature but, at low temperatures, nonlinearity of the VACs manifests at higher voltages, which is explained by the higher resistance on the barrier. With the growth in the temperature in the semiconductor layer near the barrier, the electrons are excited to higher levels and the probability of the passage through the barrier increases, which leads to a decrease in the region of ohmicity. Thermal breakdown is the main breakdown mechanism in this region.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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