BROOKHAVEN
NATIONAL LABORATORY

BNL-81885-2008-CP

Good electrical contacts for high resistivity (Cd,Mn)Te crystals

M. Witkowska-Baran, A. Mycielski, D. Kochanowska, A. J. Szadkowski, R. Jakiela, B. Witkowska, W. Kaliszek, J. Domagala, E. Lusakowska, V. Domukhovski, K. Dybko, Y. Cui and R. B. James

Presented at the IEEE Dresden 2008
Nuclear Science Symposium Medical Imaging Conference
Dresden, Germany
October 19-25, 2008

October 2008

Nonproliferation and National Security Department
Brookhaven National Laboratory
P.O. Box 5000
Upton, NY 11973-5000
www.bnl.gov

DISCLAIMER

Good electrical contacts for high resistivity (Cd,Mn)Te crystals

M. Witkowska-Baran, A. Mycielski, D. Kochanowska, A. J. Szadkowski , R. Jakieła, B. Witkowska, W. Kaliszek , J. Domagała, E. Łusakowska, V. Domukhovski, K. Dybko, Y. Cui and R. B. James

***Abstract*– We consider that semi-insulating (Cd,Mn)Te crystals may well successfully replace the commonly used (Cd,Zn)Te crystals as a material for manufacturing large-area X- and gamma-ray detectors. The Bridgman growth method yields good quality and high-resistivity (10^9 ~ 10^{10} Ω·cm) crystals of (Cd,Mn)Te:V. Doping with vanadium (≈10^{16} cm^{-3}), which acts as a compensating agent, and annealing in cadmium vapors, which reduces the number of cadmium vacancies in the as-grown crystal, ensure this high resistivity.**

Detector applications of the crystals require satisfactory electrical contacts. Hence, we explored techniques of ensuring good electrical contacts to semi-insulating (Cd,Mn)Te crystals. Our findings are reported here.

Before depositing the contact layers, we prepared an "epi-ready" surface of the crystal platelet by a procedure described earlier for various tellurium-based II–VI compound crystals. A molecular beam epitaxy (MBE) apparatus was used to deposit various types of contact layers: Monocrystalline semiconductor layers, amorphous- and nanocrystalline semiconductor layers, and metal layers were studied. We employed ZnTe heavily doped (≈10^{18} cm^{-3}) with Sb, and CdTe heavily doped (≈10^{17} cm^{-3}) with In as the semiconductors to create contact layers that subsequently enable good contact (with a narrow, tunneling barrier) to the Au layer that usually is applied as the top contact layer.

We describe and discuss the technology and some properties of the electrical contacts to semi-insulating (Cd,Mn)Te.

INTRODUCTION

Detector applications of (Cd,Mn)Te crystals require good electrical contacts, and this communication reports our research on a technique of making good electrical contacts to semi-insulating (Cd,Mn)Te crystals. "Good" contacts are those that have the following characteristics:

1. Do not block the transport of at least one type of current carrier;
2. Have linear current-voltage characteristics; and
3. Keep small portion of the voltage applied to the sample with contacts (i.e., "contact resistance" is small).

To date, only a gold layer chemically deposited directly onto the crystal surface has been used as the electrical contact to semi-insulating (Cd,Mn)Te crystals [1][2].

Equipment for characterization measurements

We employed a molecular beam epitaxy (MBE) apparatus to deposit various monocrystalline, amorphous, and nanocrystalline layers. We investigated the quality of the crystal structure by X-ray diffraction spectroscopy equipped with a Siemens D-5000 diffractometer, and by "rocking curve" measurements. The surfaces of the crystal plates and contact layers were studied with a Secondary Ion Mass Spectrometer (SIMS) - CAMECA IMS6F, and with an Atomic Force Microscope (AFM) working in Tapping Mode. With a Keithley 617 Programmable Electrometer, we measured resistances and the current-voltage characteristics of the contact structures.

Manuscript received November 14, 2008. The work was partially funded by the Polish Ministry of Science and Higher Education through grant 3 T08A 046 30.

M. Witkowska-Baran (e-mail: mwitkow@ifpan.edu.pl), A. Mycielski, D. Kochanowska, A. J. Szadkowski , R. Jakieła, B. Witkowska, W. Kaliszek , J. Domagała, E. Łusakowska, V. Domukhovski and K. Dybko are with the Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 32/46, 02-668 Warsaw, Poland.

Y. Cui and R.B. James are at the Brookhaven National Laboratory, Upton, NY 11973, USA.

Crystals

Semi-insulating crystals are needed for application in detectors. We grew good-quality, high-resistivity ($10^9 \sim 10^{10}$ Ω-cm) single crystals of (Cd,Mn)Te:V by the Bridgeman method.

The crystals' high resistivity was assured by doping with vanadium, which acts as a compensating material, and special annealing in cadmium vapors, which reduces the number of cadmium vacancies existing in the as-grown crystal.

We studied compensation of (Cd,Mn)Te crystals with vanadium concentrations ranging from $3 \cdot 10^{16}$ to $5 \cdot 10^{17}\text{cm}^{-3}$; the optimum compensation was achieved very close to 10^{16} cm^{-3}.

Annealing the crystal platelets in cadmium vapors decreases the concentration of cadmium vacancies existing in the crystal [3], and the number of tellurium precipitates. Another publication describes this phenomenon [4].

Crystal plates

Cd-annealed, high-resistivity crystal plates usually are about 30 mm × 30 mm × 2.5 mm. The large surfaces of the plates are parallel to the (111) crystal planes. Smaller samples, 3 mm × 3 mm × 1.2 mm, were used for testing the contacts.

Before depositing the contact layers, we prepared "epi-ready" surfaces of the crystal plates following a procedure described for various tellurium-based II–VI compound crystals [3] and [5]. The exception here was that we chemically deposited Au directly on the surface.

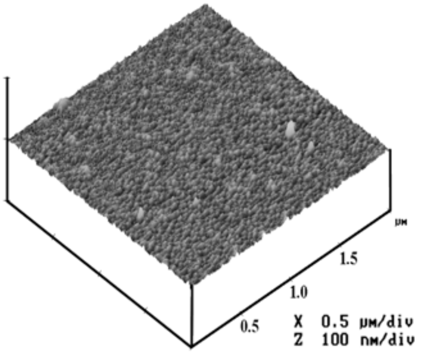

Fig. 1. Roughness of the "epi-ready" surface of a (Cd,Mn)Te plate (atomic force microscopy data). The Root Mean Square Roughness is 1.6 nm.

The final process in preparing the "epi-ready" (Fig. 1) surface was the special etching that creates a tellurium-rich layer, about 30 Å thick. Fig. 2 illustrates the distribution of atoms in this modified layer that protects the crystal surface from oxidizing too quickly before the next technological steps.

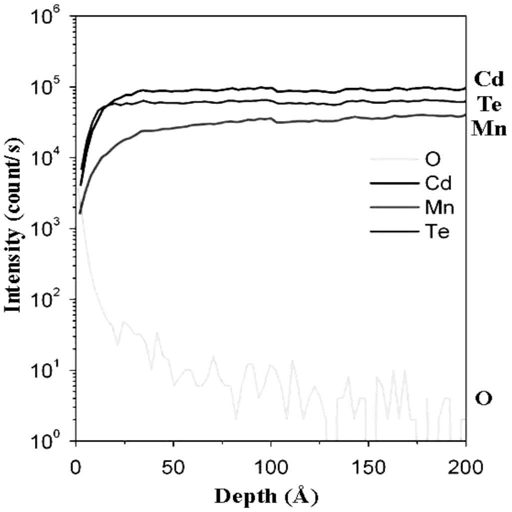

Fig. 2. Distribution, obtained by SIMS analysis, of atoms near the surface of a (Cd,Mn)Te crystal plate after special etching. A layer with an accumulation of anions and depletion of cations exists near the surface and protects the surface against further oxidation.

Contact layers

Our investigations were concentrated on three approaches to making electrical contacts to the high-resistivity (Cd,Mn)Te crystals:

1. A metal (Au) layer is chemically deposited directly onto the crystal's surface;
2. A monocrystalline layer of a heavily doped semiconductor is deposited onto the crystal's surface by an MBE process (and then covered with an Au layer);
3. An amorphous or nanocrystalline layer of a heavily doped semiconductor is deposited onto the crystal surface by evaporation (and then covered with an Au layer).

Since the layers of heavily doped semiconductors subsequently were covered with an Au layer, we followed standard methods of connecting external circuits to the Au layer.

As the outermost layer of the contact structure usually is a metal (Au) deposited on the surface of proper semiconductor, it is valuable to recall the properties of the interface between a semiconductor and a metal.

Almost invariably, the bands in the semiconductor are bent near the interface (determined by the work functions, surface states, and density of localized states in the semiconductor) and near barriers (like the Schottky barrier), blocking the transport of electrons or holes.

However, in a heavily doped semiconductor (with a large density of localized states), the barriers are very thin and the current carriers can flow through them due to tunneling; then, the contact is good.

In selecting semiconductors for making contact layers to high-resistivity crystals intended for radiation detectors, it is not necessary to make two "universally" good contacts (for electrons and holes) on the opposite sides of the crystal plate. Because of the principles of operation of a detector, it is enough to prepare one contact, which is good for transport of electrons (out of the plate), and the other for holes.

Au layer chemically deposited onto the crystal surface

All the surfaces of a crystal plate were ground (powder: 20 ÷ 30 μm) and washed. Then, the plate was etched in the mixture of bromine (10 vol. %) and methanol, and washed again. Au was chemically deposited from the $AuCl_3 \cdot HCL \cdot 4H_2O$ (gold chloride acid) + H_2O_2 (distilled) solution in a reaction between this solution and the crystal's surface.

The current-voltage characteristics were measured for current flowing between two Au-electrodes (Figs. 3 and 4). Standard four-probe measurements were taken with an electrometer (with very high input impedance) to determine the material's resistivity.

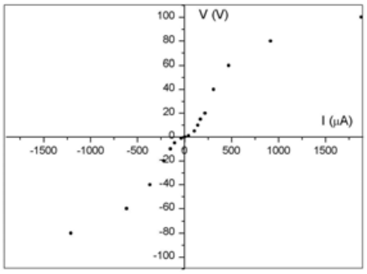

Fig. 3. Current-voltage characteristic for the current between two Au contacts on $Cd_{0.91}Mn_{0.09}Te$:V ($3 \cdot 10^{16}$ cm^{-3}) sample No. 4561.

While electrical contacts made by evaporating Au onto the (Cd,Mn)Te surface usually are poor (very nonlinear) (Fig. 3) due to barriers between Au and the crystal, sometimes the chemical deposition of Au gives good results (Fig. 4), and the current-voltage characteristics are almost linear.

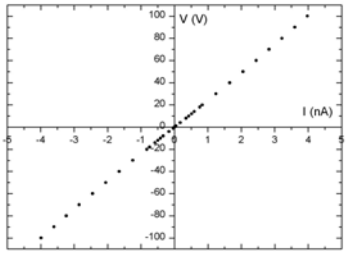

Fig. 4. Current-voltage characteristic for the current between two Au contacts on $Cd_{0.95}Mn_{0.05}Te$:V ($5\cdot10^{16}$ cm^{-3}) sample No. 4512. The resistivity of the sample was $2.5\cdot10^{9}$ Ω-cm.

Nevertheless, this method of making contacts is not easily repeatable and cannot be used for detector manufacturing purposes.

Monocrystalline layer of a heavily doped semiconductor deposited on to the crystal surface by an MBE process

Rioux, Niles and Höchst [6] achieved good contacts to a p-type CdTe crystal by growing a monocrystalline layer of ZnTe (Fig. 5), heavily doped with Sb, on its properly prepared surface. Following their approach, we grew, in an MBE apparatus, monocrystalline layers (about 0.5 ~ 1 µm thick) of heavily-doped semiconductors on epi-ready surfaces of high-resistivity (Cd,Mn)Te crystals. We used as the contact layers ZnTe heavily doped ($\approx10^{18}$ cm^{-3}) with Sb, and CdTe heavily doped ($\approx10^{17}$ cm^{-3}) with In.

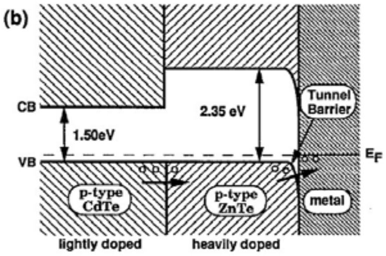

Fig. 5. Thin, tunnelling barrier between the outer metal layer and the heavily doped p-type ZnTe monocrystalline layer used as the contact layer to a p-type CdTe crystal. [6]

Using atomic force microscopy (AFM), we studied the "epi-ready" surface (Fig. 6) of a (Cd,Mn)Te crystal and the surface of the contact layer (Fig. 7). The “root mean square” (RMS) roughness was 1.6 nm for the epi-ready (Cd,Mn)Te surface, and 1.95 nm for the 1-µm thick ZnTe:Sb ($5\cdot10^{18}$ cm^{-3}) contact layer [5].

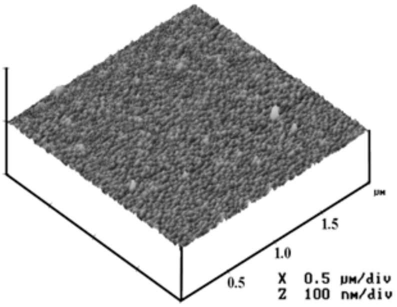

Fig. 6. Roughness of the "epi-ready" surface of a (Cd,Mn)Te plate (atomic force microscopy data).

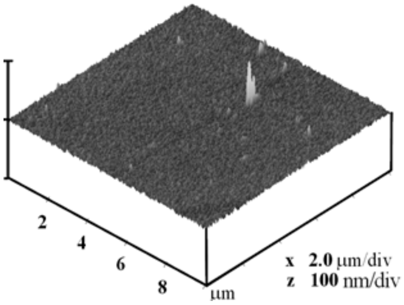

Fig. 7. Roughness of the the ZnTe:Sb layer grown on the "epi-ready" surface of a (Cd,Mn)Te plate (atomic force microscopy data).

X-ray diffraction was measured for the ZnTe:Sb contact layers grown on the (Cd,Mn)Te (111) crystal plates; Fig. 8 shows the results. The sharp lines of the refluxes from the monocrystalline contact layer are apparent. [5]

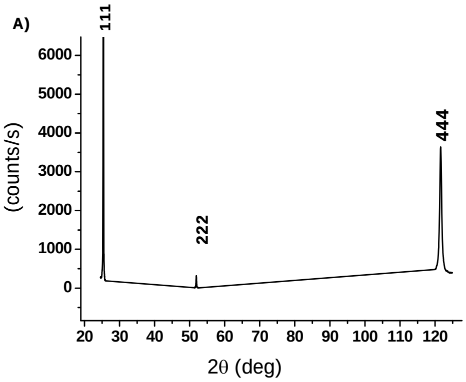

Fig. 8. Diffraction spectrum for single crystal layer of ZnTe:Sb grown on the (Cd,Mn)Te monocrystalline plate. [5]

The quality of the crystal structure of the ZnTe:Sb contact layers was determined by "rocking curve" measurements. The "full width at half maximum" (FWHM) of the (111) rocking curve was 43 arc-sec for the monocrystalline ZnTe:Sb contact layer, and 68 arc-sec for the underlying (Cd,Mn)Te crystal plate.

In Fig. 9, we give an example of the current-voltage characteristic for the current flowing between two monocrystalline ZnTe:Sb ($5\cdot10^{18}$ cm^{-3}) contact layers on a (Cd,Mn)Te crystal plate. The resistivity of the (Cd,Mn)Te crystal was $2\cdot10^{6}$ Ω-cm. The current-voltage characteristic is linear for voltages between –50 V and +50 V [5].

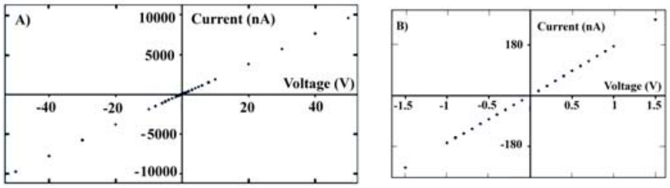

Fig. 9. Current-voltage characteristic for the current flowing between two ZnTe:Sb ($5\cdot10^{18}$ cm^{-3}) monocrystalline contact layers grown on the (Cd$_{0.87}$Mn$_{0.13}$Te:V crystal plate. The resistivity of sample was $2\cdot10^{6}$ Ω-cm. A), and B) the same characteristic shown in two different voltage ranges. [5]

The proper monocrystalline semiconductor layers can serve as electrical contacts to high-resistivity (Cd,Mn)Te crystals, but for very limited range of applications. They cannot be used for typical radiation detectors (especially pixellated detectors), where contacts have to be made on the opposite sides of the crystal plate. The reason lies in the detrimental effect of the second process of epitaxy (for making the contact layer on the second face) on the contact layer already deposited on the first face of the plate. The processes require the temperature of the sample holder to be about 300 °C.

Amorphous or nanocrystalline layer of a heavily doped semiconductors between the crystal and Au

Sebestyen [7] (see also [8]) suggested using amorphous /nanocrystalline layers of heavily doped semiconductors instead of epitaxial (monocrystalline) layers. (Sometimes it is difficult to distinguish between an amorphous layer and a nanocrystalline one).

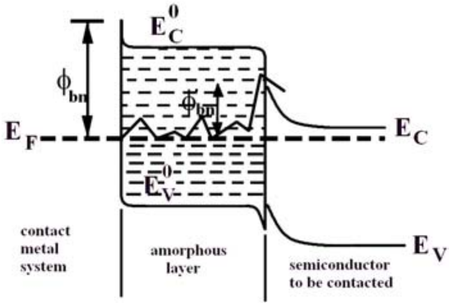

Fig. 10. Amorphous layer with uniform mobility gap used as the intermediate contact layer between the semiconductor crystal and the metal. The electrons flow due to hopping through the amorphous layer and to tunnelling through, or passing over the barrier. E_C^0 and E_V^0 – the mobility gap edges. After [8].

Figs. 10 and 11 represent Sebestyen's ideas. They depict the band diagrams of the crystal with the contact structures.

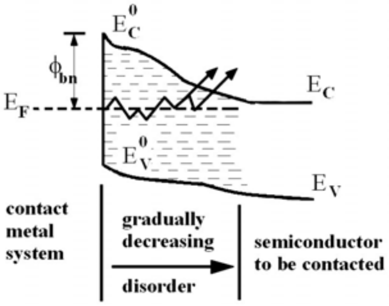

Fig. 11. Amorphous layer with graded mobility gap used as the intermediate contact layer between the semiconductor crystal and the metal. Through the amorphous layer the electrons flow due to hopping (as in Fig. 10), but there is almost no barrier between the amorphous layer and the metal. The meaning of the symbols is the same as in Fig. 10. [8]

An abrupt junction between the amorphous semiconductor and the crystal semiconductor generally offers some associated barrier to the flow of current carriers. However, this barrier may disappear if the degree of disorder gradually decreases from the metal towards the crystalline surface (Fig. 10) [8].

Inside the amorphous contact layers, the current flows mainly due to electron hopping between the localized states -- the energy levels of which lie near the Fermi level.

The p-type ZnTe:Sb and n-type CdTe:In amorphous /nanocrystalline contact layers were evaporated on the "epi-ready" surfaces of the semi-insulating (Cd,Mn)Te crystal plates with an MBE machine that functioned as a very good evaporating apparatus (Fig. 12). ZnTe was deposited on the Cd-side of the plates, CdTe – on the Te-side. During evaporation, the temperature of the crystal plate was about 80-90 °C; thus, the second evaporation did not ruin the layer deposited first.

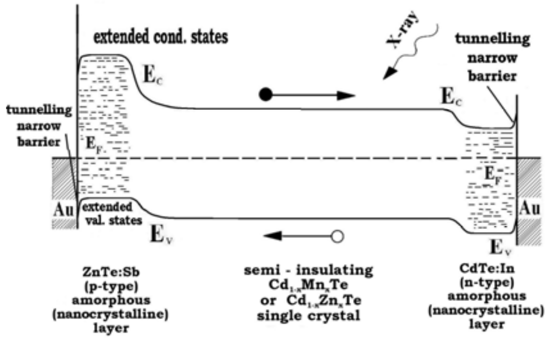

Fig. 12. System of electrical contacts to the high-resistivity (Cd,Mn)Te plate to be used as radiation detector. The ideas of Sebestyen were followed. The amorphous layers of p-type ZnTe:Sb and n-type CdTe:In were evaporated onto the epi-ready surfaces of the (Cd,Mn)Te crystal.

The generated layers were amorphous or nanocrystalline (the size of the crystallites was below 10 nm). Finally, a gold layer was evaporated onto the contact layers.

To obtain thin, tunneling, barriers between the semiconductor and Au layer (to establish a good contact) the semiconductor possibly should be doped heavily doped. Concentrations of the dopants (Sb and In) in our amorphous /nanocrystalline contact layers were about 10^{18} cm^{-3}. The surfaces of the contact layers evaporated onto the (Cd,Mn)Te crystal were studied by atomic force microscopy (AFM). Figs. 13 and 14 present the findings from analyses of surface roughness of these two types of contact layers.

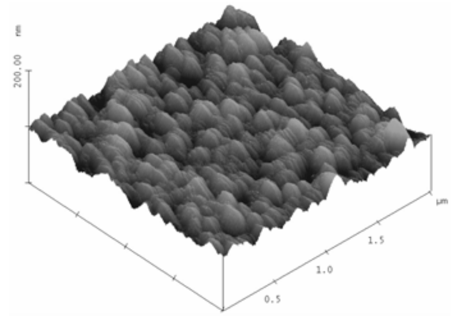

Fig. 13. Roughness of the 1 µm thick CdTe:In contact layer deposited on the surface of a (Cd,Mn)Te plate (atomic force microscopy data). The Root Mean Square (RMS) roughness is 8.812 nm.

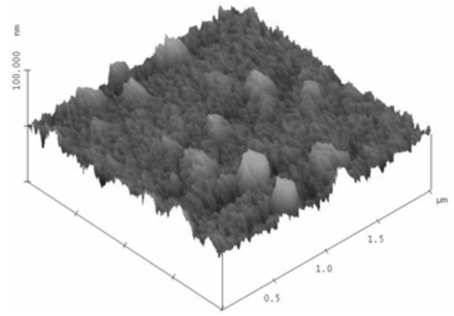

Fig. 14. Roughness of the 1 µm thick ZnTe:Sb (≈10^{18} cm^{-3}) contact layer deposited on the surface of a (Cd,Mn)Te plate (atomic force microscopy data). The Root Mean Square (RMS) roughness is 10.948 nm.

The current-voltage characteristics for the current flowing between the pairs of contacts were measured at room temperature. The structure of the contacts in tests for the I-V measurements is shown in Fig. 15.

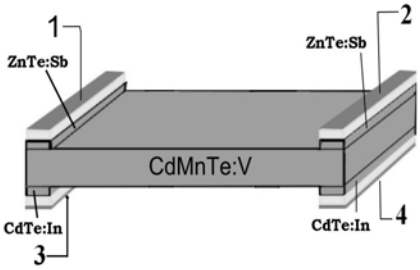

Fig. 15. System of electrodes for testing contacts. Amorphous layers of ZnTe:Sb (≈10^{18} cm^{-3}) and CdTe:In (≈10^{17} cm^{-3}) are deposited on the opposite sides of the (Cd,Mn)Te:V plate.

The results of measurement from these tests are shown in Figs. 16 and 17.

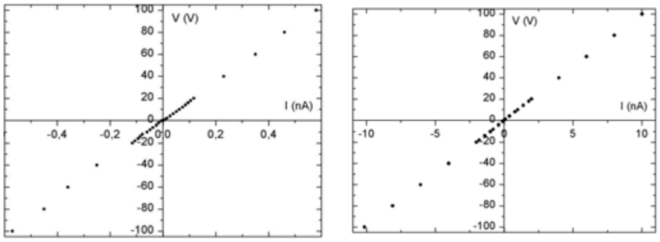

Fig. 16. Current-voltage characteristic for the current flowing between two ZnTe:Sb contacts: 1 and 2 (left), 3 and 4 (right). $Cd_{0.95}Mn_{0.05}Te$:V ($5\cdot10^{15}$ cm^{-3}) crystal plate.

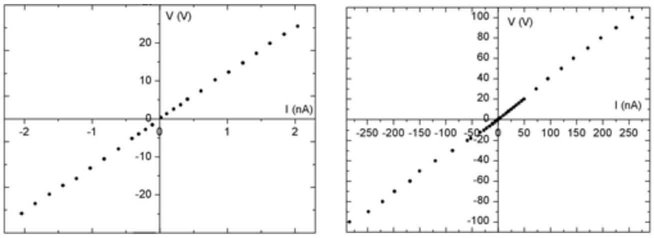

Fig. 17. Left graph - current-voltage characteristic for the current flowing between two ZnTe:Sb contacts (1 and 4). $Cd_{0.95}Mn_{0.05}Te$:V ($5\cdot10^{15}$ cm^{-3}) crystal plate. Right graph - current-voltage characteristic for the current flowing between the ZnTe:Sb contact (2) and the CdTe:In contact (3). $Cd_{0.95}Mn_{0.05}Te$:V ($5\cdot10^{15}$ cm^{-3}) crystal plate.

As seen in Figs. 16 and 17, the current-voltage characteristics are linear for the current flowing between the electrodes prepared by the technique discussed here. Many samples with contact structures were prepared, and the I-V characteristics were measured, and in about 95% of cases, the characteristics were linear.

Accordingly, we consider that the evaporation of amorphous/nanocrystalline layers of proper heavily-doped semiconductors onto the surface of the (Cd,Mn)Te crystal is an excellent method of making good contacts.

Conclusions

Our findings suggest that the best electrical contacts to semi-insulating (Cd,Mn)Te crystal plates are amorphous or nanocrystalline layers of proper heavily-doped semiconductors, evaporated in very high vacuum onto the "epi-ready" surface of the crystal, and subsequently covered with Au layer. The methodology and the resulting contacts also are suitable for practical applications.

Acknowledgment

The work was partially funded by the Polish Ministry of Science and Higher Education through grant 3 T08A 046 30, and by the U.S. DOE Office of Nonproliferation Research and Development, NA22.

References

[1] A. Burger, M. Groza, Y. Ciu, U. N. Roy, D. Hillman, M. Guo, L. Li, G. W. Wright and R. B. James, “Development of portable CdZnTe spectrometers for remote sensing of signatures from nuclear materials”, Phys. Stat. Sol. (c) 2, no. 5, pp. 1586-1591, 2005.

[2] A. Burger, K. Chattopadhyay, H. Chen, J. O. Ndap, X. Ma, S. Trivedi, S. W. Kutcher, R. Chen and R. D. Rosemeier, “Crystal growth, fabrication and evaluation of cadmium manganese telluride gamma ray detectors,” Journal of Crystal Growth 198/199, pp. 872-876, 1999.

[3] A. Mycielski, A. Burger, M. Sowińska, M. Groza, A. Szadkowski, P. Wojnar, B. Witkowska, W. Kaliszek and P. Siffert, “Is The (Cd,Mn)Te crystal a prospective material for X-ray and γ-ray detectors ?”, Phys. Stat. Sol. (c) 2, no. 5, pp. 1578-1585, 2005.

[4] D. Kochanowska, A. Mycielski, M. Witkowska-Baran, A. Szadkowski, B. Witkowska, W. Kaliszek, Y. Cui and R. B. James “Influence of annealing on tellurium precipitates in (Cd,Mn)Te:V crystals,” This Conference Record.

[5] M. Witkowska-Baran, A. Mycielski, A. Szadkowski, E. Łusakowska, V. Domuhkovski, R. Jakieła, B. Witkowska and W. Kaliszek, “Semi-insulating (Cd,Mn)Te:V crystals: Electrical contacts,” Phys. Stat. Sol. (b) 244, no. 5, pp. 1706-1713, 2007.

[6] D. Rioux, D. W. Niles and H. Höchst, “ZnTe: A potential interlayer to form low resistance back contacts in CdS/CdTe solar cells”, J. Appl. Phys. 73, no. 12, pp. 8381-8385, 1993.

[7] T. Sebestyen, “Models for Ohmic contacts on graded crystalline or amorphous heterojunctions”, Solid State Electronics, Vol. 25, no. 7, 198, pp. 543-550, 1982.

[8] C. J. Palmstrem and D. V. Morgan, “Gallium Arsenide Materials, Devices & Circuits,” edited by M. J. Howes and D. V. Morgan (Chichester, UK Wiley), 1985, pp. 200-205.