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Contacts for high-resistivity (Cd,Mn)Te crystals

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Abstract— Semi-insulating (Cd,Mn)Te crystals offer a material that may compete well with the commonly used (Cd,Zn)Te crystals for manufacturing large-area X- and gamma-ray detectors [1]. The Bridgman growth method yields good quality, high-resistivity ($10^9 - 10^{10} \Omega \cdot \text{cm}$) crystals of (Cd,Mn)Te:V. Doping the as-grown crystals with the compensating agent vanadium ($\approx 10^{16} \text{ cm}^{-3}$) ensures their high resistivity; thereafter, annealing them in cadmium vapors reduces the number of cadmium vacancies. Applying the crystals as detectors necessitates having satisfactory electrical contacts. Accordingly, we explored various techniques of ensuring good electrical contacts to these semi-insulating (Cd,Mn)Te crystals, assessing metallic layers, monocrystalline semiconductor layers, and amorphous (or nanocrystalline) semiconductor layers. We found that ZnTe heavily doped ($\approx 10^{18} \text{ cm}^{-3}$) with Sb, and CdTe heavily doped ($\approx 10^{17} \text{ cm}^{-3}$) with In, proved satisfactory semiconductor contact layers. They subsequently enabled us to establish good contacts (with only narrow tunneling barriers) to the Au layer that usually constitutes the most external contact layer. We outline our technology of applying electrical contacts to semi-insulating (Cd,Mn)Te, and describe some important properties.

I. INTRODUCTION

Semiconductor Radiation Detectors (SRD) for X- and γ -rays currently are manufactured mainly from CdTe- and (Cd,Zn)Te crystals. Many authors described the technology of applying suitable electrical contacts to make detectors from those crystals, and the difficulties encountered in developing them [2,3,5-11].

The metal-semiconductor interface as an electrical contact. Applying them to the semiconductor crystal used as a radiation detector is an important area for which we need a critical understanding of

the chemical species formed, and of the inter-diffusion between the metal and semiconductor, the formation of defects, and their interactions with the latter. In many cases, these factors have profound technological implications on the detector's response. Thus, several contact-related problems must be solved in developing high-efficiency, high-sensitivity (Cd,Zn)Te and CdTe detectors [3].

The same needs apply to detectors made from the proposed new material (Cd,Mn)Te; having a repeatable technology for making good electrical contacts is essential.

There is much less research on contacts to (Cd,Mn)Te; gold and aluminum were suggested as the contact metals [12,13]. Zhang [12] studied chemically deposited Au contacts on low-resistivity crystals (about $10^5 \Omega \cdot \text{cm}$), obtaining ones with linear current-voltage characteristics. Kim et al. [13] recorded linearity with a high ($10^{10} \Omega \cdot \text{cm}$) resistivity (Cd,Mn)Te for electron-beam-evaporated Au.

The apparent ambiguity in results obtained so far led us to further investigate traditional materials and completely new ones in attempting to achieve nearly ohmic contacts to semi-insulating (Cd,Mn)Te.

Nearly Ohmic Contacts (NOCs) are those with the following properties:

1. They do not block the transfer of current carriers, as manifested characteristically by a non-linear current-voltage characteristic, in particular, the transfer of additional carriers excited by radiation.
2. They retain only a small portion of the voltage applied to the sample with contacts, i.e., their "contact resistance" is small.
3. Accordingly, they have a linear current-voltage characteristic down to very small voltages (e.g., 50 mV).

II. CRYSTALS

We grew good-quality, high-resistivity ($10^9 - 10^{10} \Omega \cdot \text{cm}$) single crystals of (Cd,Mn)Te:V by the Bridgman method. We ensured their high resistivity by doping them with vanadium, a compensating dopant, in concentrations ranging from 3×10^{16} to $5 \times 10^{17} \text{ cm}^{-3}$, and then annealing them in cadmium vapors that reduces the concentration of cadmium vacancies in the as-grown crystal [1]. Moreover, it lowers the number of tellurium inclusions and precipitates, as described by Kochanowska et al. [14].

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III. CRYSTAL PLATES AND SAMPLES

We cut plates $30\text{ mm} \times 30\text{ mm} \times 2.5\text{ mm}$ from the high-resistivity crystals; their large surfaces were parallel to the crystal's (111) planes. We employed smaller samples, $3\text{ mm} \times 3\text{ mm} \times 1.2\text{ mm}$, for testing the contacts.

There are many aspects to preparing a crystal surface before depositing the contact layers. Wang [5] demonstrated the influence of surface roughness, showing that, for good results, the "root mean square" (RMS) roughness should not exceed 50 nm.

Our measurement of the roughness of a (Cd,Mn)Te crystal's surface (with an accumulation layer of Te) by atomic force microscopy (AFM) gave a value of 1.6 nm.

Preparing of the crystal's surface for depositing the contact layers differed for various contact layers.

1. The following processes preceded the chemical deposition of Au as the only contact layer:

- Grinding with SiC 20- μm powder,
- Mechanochemically polishing in a 2% solution of Br in methanol + glycol,
- Etching in a 9% solution of Br in methanol, and,
- Thoroughly rinsing in methanol.

Thereafter, Au was chemically deposited from a solution of $\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$ (gold chloride acid + distilled H_2O_2) in a reaction between the solution and the crystal's surface.

2. The deposition of monocrystalline semiconductor contact layers, accomplished in a molecular beam epitaxy (MBE) apparatus, was preceded by the following steps:

- Grinding with SiC 20- μm powder,
- Mechanochemically polishing in a 2% solution of Br in methanol + glycol,
- Selective etching (15 s) in a 0.1% solution of Br in methanol, and,
- Thoroughly rinsing in methanol.

Selective etching removes Cd at the surface and leaves an accumulation layer of Te.

For depositing a contact layer we needed a surface of the crystal wherein the Cd:Te ratio was stoichiometric. When there is a layer of Cd at the surface, it quickly becomes oxidized, and then is difficult to remove, even when heated in a vacuum up to 350 °C. In contrast, an accumulation layer of Te readily is removed by heating under vacuum. We prepared the ideal surface as far as possible, i.e., one suitable for epitaxy.

For molecular beam epitaxy of II-VI materials, such a surface with an accumulation layer of tellurium, which is removed straightforwardly in the MBE machine by heating above 300 °C, usually is termed "epi-ready".

3. Deposition of amorphous semiconductor contact layers (in the MBE apparatus) was anteceded by the same procedure used for the monocrystalline contact layers, except that the accumulation layer of Te was not evaporated away.

Selective etching creates a tellurium-rich layer, about 20-Å thick. Fig. 1 illustrates the distribution of atoms in this layer.

Fig. 1. Distribution, obtained by SIMS analysis, of atoms near the surface of a (Cd,Mn)Te crystal plate after etching. A layer with an accumulation of anions, but depleted of cations exists near the surface.

This type of etching is detailed in [1] and [15].

IV. EQUIPMENT FOR MEASUREMENTS

We employed an MBE apparatus to deposit various monocrystalline, amorphous, or nanocrystalline layers. X-ray diffraction spectroscopy with a Siemens D-5000 diffractometer and "rocking curve" measurements revealed the quality of the crystals. We explored the surfaces of the crystal plates and contact layers with a Secondary Ion Mass Spectrometer (SIMS), CAMECA IMS6F, and with an Atomic Force Microscope (AFM) working in the tapping mode. We used a Keithley 617 Programmable Electrometer with very high input resistance ($> 10^{14} \Omega$) and with an internal voltage source (up to 100 V) to measure the current-voltage characteristics and the resistivity of crystals with different contact structures. We mapped the resistivity in the large crystal plates by a contactless method with a EU-p SCAN (Scanning analyzer of the X-ray detector crystals).

IV. CURRENT – VOLTAGE CHARACTERISTICS

We determined the current-voltage characteristics for three types of contact layers:

- Chemically deposited Au layer,
- MBE-deposited monocrystalline semiconductor layer, and,
- Evaporated amorphous or nanocrystalline semiconductor layer.

Figs. 2 a) and b) present the geometry of the electrodes for measuring the current-voltage characteristic (I-V curves). In these "two-electrode" measurements, the applied voltage is distributed between the first contact region, the bulk, and the second contact region.

Fig. 2. Geometry of electrodes for measuring the current-voltage characteristics. Current flow is represented by I , and voltage by V .

In Fig. 2(a) the electrodes are placed on the same side of the sample (its upper side, as shown in Fig. 3), whilst in fig. 2(b) the electrodes are on the opposite sides of the crystal plate, as in many types of planar radiation-detectors. The resulting voltage is the sum of voltages on the first contact, on the bulk, and on the second contact.

Fig. 3. A sample with electrodes for the "two-electrode measurement" of the I-V characteristics.

To measure the characteristics of one contact, we employed the geometry of the "three-electrode measurement" depicted in Fig 4; however, electrode 3 was irrelevant in this measurement. The current I flowed between electrodes 1 and 4, and the voltage $V_{1,2}$ was measured between electrodes 1 and 2. Due to the electrometer's very high resistance, no current flowed through electrode 2, and its presence did not disturb the current I flowing through contact 1. In this approach, the voltage $V_{1,2}$ is the sum of the voltage on contact 1 (related to the "contact resistance"), and the voltage on the crystal between contact 1 and the position of electrode 2.

Fig. 4. A sample with electrodes for the "three-electrode measurement" of the I-V characteristics, and for the "four-electrode measurement" of resistivity.

All four electrodes (Fig. 4) were used for the standard "four-electrode measurement" of the crystal's resistivity. For this purpose, we took one value of the voltage V between probes 2 and 3 (for one value of the current I). We also determined the voltage between these same probes as a function of the current I . This determination of the characteristic does not involve the properties of the contacts; nevertheless, nonlinearities of this characteristic can reveal non-uniformities in the region of the crystal between probes 2 and 3. Fig. 5 illustrates a sample with the electrodes for the "three-electrode measurement" of I-V characteristics.

Fig. 5. Sample with electrodes for "three-electrode measurement" of the current-voltage characteristics, and for the standard "four-electrode

measurement" of the crystal's resistivity. The semiconductor contact layers are shown.

Usually, high-resistivity (Cd,Mn)Te is very photosensitive, so we kept the samples in the dark while measuring the I-V characteristics and resistivity. The surface of the samples between the electrodes was etched with a mixture of bromine (9 vol. %) and methanol to suppress surface-leakage currents.

The existence of additional currents flowing along the surface was investigated via guard-ring measurements, wherein surface currents are eliminated, and only the current flowing through the bulk is measured. After treating the surface with this etchant, we found no significant contribution from surface currents for typical configurations of the electrodes.

V. CONTACT LAYERS

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

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

1. Au layer chemically deposited onto the crystal's surface

All the surfaces of a crystal plate were prepared in the way described above. We measured the current-voltage characteristics for the current flowing between the two Au-electrodes (Figs. 6 and 7).

Fig. 6. Current-voltage characteristic for the current between two Au contacts on the $\text{Cd}_{0.93}\text{Mn}_{0.07}\text{Te}:\text{V}$ ($5 \cdot 10^{15} \text{ cm}^{-3}$). The average resistivity of the material was about $10^9 \Omega \cdot \text{cm}$.

Fig. 7. Current-voltage characteristic for the current between two Au contacts on the $\text{Cd}_{0.87}\text{Mn}_{0.13}\text{Te}:\text{V}$ ($5 \cdot 10^{16} \text{ cm}^{-3}$). The average resistivity of the material was about $10^9 \Omega \cdot \text{cm}$.

To determine the material's resistivity, we acquired standard four-electrode measurements with an electrometer.

The electrical contacts made by evaporating Au onto the (Cd,Mn)Te surface are known to be very nonlinear due to the barriers between the Au and the crystal; the same often is true for chemically deposited Au, as is apparent in Figs. 6 and 7. Sometimes chemically deposited Au gives good results, and the current-voltage characteristics are almost linear (Fig. 8).

Fig. 8. Example of good contacts to (Cd,Mn)Te crystals. Current-voltage characteristic for the current between two Au contacts on $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te}:\text{V}$ ($5 \cdot 10^{16} \text{ cm}^{-3}$). The resistivity of the material was $3 \cdot 10^9 \Omega \cdot \text{cm}$.

Chemically depositing Au onto the surface of (Cd,Mn)Te does not create an abrupt interface between them. Rather, the chemical reaction generates a complex interlayer, usually about 1- μm thick. Musa et al. [10] described the process of creating it. Depending on the conditions during preparation, this layer's electronic properties may enable the easy flow of current carriers between Au and the crystal, i.e., a good, nearly ohmic contact is made.

However, at least for our (Cd,Mn)Te crystals, the preparation of the Au-contacts by chemical deposition and by evaporation was unrepeatable, and hence, cannot be used in manufacturing detectors.

Thus, from 30 samples with chemically deposited Au-contacts, only 18 presented linear I-V characteristics, while only one did so from 10 samples fabricated with evaporated Au-contacts. For both groups, the samples' parameters were very similar, and the technology of making the contacts was nominally identical.

2. Monocrystalline layer of a heavily doped semiconductor deposited onto the crystal surface by an MBE process

Rioux, Niles, and Höchst [16] reportedly achieved good contacts to a p-type CdTe crystal by growing a monocrystalline layer of ZnTe, heavily doped with Sb, on its prepared surface.

Fig. 9. Heavily doped p-type ZnTe monocrystalline layer used as the contact layer to the semi-insulating (Cd, Mn)Te crystal. The holes easily tunnel across the thin barrier between ZnTe and the outermost metal layer.

Following their approach (Fig. 9), we grew, in an MBE apparatus, monocrystalline layers (about 0.5 - 1 μm thick) of heavily doped semiconductors on the "epi-ready" surfaces of high-resistivity (Cd,Mn)Te crystals. We used as the contact layers ZnTe heavily doped (10^{18} cm^{-3}) with Sb (p-type material), and CdTe heavily doped (10^{17} cm^{-3}) with In (n-type material). We checked, by Hall-effect measurements, the concentration of the current carriers in those doped semiconductor layers. To confirm the monocrystallinity of the contact layers, we collected X-ray diffraction spectra from the ZnTe:Sb contact layers grown on the (Cd,Mn)Te (111) crystal plates. Fig. 10 shows the sharp lines of the reflections from the monocrystalline contact layer. [15]

Fig. 10. X-ray diffraction spectrum for the monocrystalline layer of ZnTe:Sb (for (111), (222) and (444)) grown on the (Cd,Mn)Te (for (333)) crystal plate. [15].

The quality of the crystal structure of the monocrystalline 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, and was 68 arc-sec for the underlying (Cd,Mn)Te crystal plate. In Fig. 11, we illustrate an example of the current-voltage characteristics for the current flowing between two monocrystalline ZnTe:Sb ($3 \cdot 10^{18} \text{ cm}^{-3}$) contact layers on the same side of a (Cd,Mn)Te

crystal plate. It is linear for voltages between -100 V and $+100$ V.

Fig. 11. Current-voltage characteristic for the current flowing between two ZnTe:Sb ($5 \cdot 10^{18} \text{ cm}^{-3}$) contacts (two areas of the monocrystalline layer grown on the same side of a (Cd,Mn)Te:V crystal plate). The average resistivity of the material was about $10^9 \Omega \cdot \text{cm}$.

Whilst monocrystalline semiconductor layers can serve as electrical contacts to high-resistivity (Cd,Mn)Te crystals, they have a very limited range of applications. They are unsuitable for typical radiation detectors, especially pixelated ones, where the contacts must be made on opposite sides of the crystal plate because of the detrimental effect of the second process of epitaxy (in making the contact layer on the second face) on the contact layer already deposited on the plate's first face. In addition, a second exposure to temperatures above 350°C (which occurs during the second epitaxial growth of a $1\text{-}\mu\text{m}$ -thick layer) changes the structural- and electrical-properties of the monocrystalline layer deposited previously.

3. Amorphous or nanocrystalline layer deposited on a heavily doped semiconductor between the crystal and Au layer

Sebestyen [17] suggested using amorphous/nanocrystalline layers of heavily doped semiconductors instead of epitaxial (monocrystalline) layers (see subsequent work in [18]). Sometimes, it is difficult to distinguish between an amorphous layer and a nanocrystalline layer. Inside amorphous contact layers, the flow of current mainly reflects electron hopping between the localized states, the energy levels of which lie near the Fermi level. Following Sebestyen's approach, we evaporated p-type ZnTe:Sb and n-type CdTe:In amorphous/nanocrystalline contact layers on the (tellurium-enriched) surface of semi-insulating (Cd,Mn)Te crystal plates (Fig. 12) employing an MBE machine that functioned well for this task.

The vacuum in the chamber was about 10^{-6} - 10^{-8} Torr. During evaporation, the temperature of the crystal plate was about 80°C ; thus, the second evaporation did not ruin the previously deposited layer.

Fig. 12. System of establishing electrical contacts for the high-resistivity (Cd,Mn)Te plate intended as a radiation detector. 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.

ZnTe was deposited on the Cd-side (A-side) of the plates, and CdTe on the Te-side (B-side), a choice substantiated by Herman and Sitters' [19] discussion of the epitaxial growth of II-VI compounds. Finally, a gold layer was evaporated on top of the contact layers. The concentrations of the dopants (Sb and In) in the contact layers were about 10^{17} - 10^{18} cm^{-3} . Due to this high level of doping, only a thin, tunneling barrier existed between the semiconductor near-surface region and the outer gold layer, enabling good contact there, just as in the case of monocrystalline contact layers. We then characterized the ZnTe:Sb and CdTe:In contact layers via the Hall effect and resistivity measurements. For both compounds, the concentration of current carriers was about 10^{17} cm^{-3} , mobility was $\sim 100 \text{ cm}^2/\text{V}\cdot\text{s}$, and resistivity ranged from 80 - $160 \Omega \cdot \text{cm}$. The contact layers were amorphous or nanocrystalline, with nano-crystallite sizes below 10 nm , as we confirmed with X-ray diffraction measurements (Fig. 13).

Fig. 13. X-ray diffraction spectrum of amorphous layers of ZnTe:Sb grown on the Cd side, and CdTe:In grown on the Te side of the (Cd,Mn)Te monocrystalline plate.

We measured the current-voltage characteristics of the contacts made by depositing the amorphous layers of the heavily doped semiconductors at room temperature. Fig. 14 illustrates the characteristic of *one* ZnTe:Sb contact (the measured voltage is the sum of the voltages on one contact, and on the adjacent piece of the crystal).

Fig. 14. Current-voltage characteristic ("three-electrode measurement" (see Fig. 4) for a ZnTe:Sb contact on a $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:V}$ (310^{16} cm^{-3}) crystal plate. The resistivity of the crystal, measured before depositing the contact layers, was $8 \cdot 10^9 \Omega \cdot \text{cm}$.

Similarly, Fig. 15 depicts the characteristic of the CdTe:In contact.

Fig. 15. Current-voltage characteristic ("three-electrode measurement" - see Fig. 4) for a CdTe:In contact on a $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:V}$ (310^{16} cm^{-3}) crystal plate. The resistivity of the crystal, measured before depositing the contact layers, was $7 \cdot 10^9 \Omega \cdot \text{cm}$.

Fig. 16 illustrates the characteristics for samples with two ZnTe:Sb contacts ("two-electrode measurement" (see Fig. 2a)).

Fig. 16. Current-voltage characteristic ("two-electrode measurement" as shown in Fig. 2a) for the current flowing between two ZnTe:Sb contacts deposited on a $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:V}$ (310^{16} cm^{-3}) crystal plate. The resistivity of the crystal, measured before depositing the contact layers, was $8 \cdot 10^9 \Omega \cdot \text{cm}$.

Fig. 17. Current-voltage characteristic ("two-electrode measurement" as shown in Fig. 2a) for the current flowing between two CdTe:In contacts deposited on a $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:V}$ ($3 \cdot 10^{16} \text{ cm}^{-3}$) crystal plate. The resistivity of the crystal, measured before depositing the contact layers, was $7 \cdot 10^9 \Omega \cdot \text{cm}$.

Similarly, Fig. 17 depicts the characteristics of a sample with two CdTe:In contacts ("two-electrode measurement").

In Fig. 18, we plot the characteristic ("two-electrode measurement") for the current flowing between two different contacts, viz., ZnTe:Sb and CdTe:In.

Fig. 18. Current-voltage characteristic ("two-electrode measurement" as shown in Fig. 2a) for the current flowing between a ZnTe:Sb contact and a CdTe:In contact deposited on a $\text{Cd}_{0.95}\text{Mn}_{0.05}\text{Te:V}$ ($5 \cdot 10^{15} \text{ cm}^{-3}$) crystal plate. The average resistivity of the material was about $10^9 \Omega \cdot \text{cm}$.

To assess the portion of the applied voltage "lost" at the contacts, i.e., contact resistance, for a few cuboid-like samples, typically $12 \text{ mm} \times 3 \text{ mm} \times 2 \text{ mm}$ equipped with electrodes on the opposite faces, we calculated their resistance from their geometry, and compared the previously measured resistivity ρ with the observed resistance (V/I) between them. The lost voltage usually was less than about 3% of the applied voltage. As our previous figures demonstrate, the current-voltage characteristics are linear for electrodes prepared by the techniques discussed in this paper, as was evident in about 95% of those we tested. Accordingly, we consider that evaporating amorphous/nanocrystalline layers of heavily doped semiconductors onto the surface of the (Cd,Mn)Te crystal is an excellent method of making nearly ohmic contacts to high resistivity crystals. However, when heavily doped ZnTe:Sb and CdTe:In are applied as amorphous contact layers, the best combination of the opposite contacts remains uncertain (i.e., Is ZnTe and ZnTe, CdTe and CdTe, or ZnTe and CdTe preferable?). We emphasize that the technology of laying down the amorphous contact layers is relatively simple. There is no need for MBE equipment; evaporation in a medium-high vacuum of about 10^{-7} - 10^{-8} Torr will suffice.

VI. CONCLUSIONS

Although contacts made by chemically depositing Au directly onto the surface of our (Cd,Mn)Te crystals sometimes seemed satisfactory, this approach is inappropriate for manufacturing radiation detectors as the process of preparing the contact is operator-dependent, and hence, often unrepeatable.

Furthermore, contacts made by MBE-growth of the monocrystalline layers of heavily doped semiconductors on the surface of (Cd,Mn)Te crystals require very complex, expensive equipment. In addition, they are extremely difficult to place on the opposite faces of the crystal plate. Thus, this technology seems to be unsuitable for manufacturing radiation detectors.

Our findings suggest that the best electrical contacts to semi-insulating (Cd,Mn)Te crystal plates are amorphous or nanocrystalline layers of appropriate heavily doped semiconductors, evaporated in a medium-to-high vacuum onto the tellurium-enriched surface of the crystal, and subsequently covered with an Au layer. We consider that this contact technology is suitable for practical applications.

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