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Ion electromigration in CdTe Schottky metal–semiconductor–metal structure

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ABSTRACT

We measured current transients in metal–semiconductor– metal (M–S–M) structure with two Au Schottky contacts fabricated to low resistivity p-CdTe material and propose a new model considering the electromigration of ions in the depletion region formed at the reversed biased Au–CdTe interface. We assume that the electric field confined in the depletion region causes at elevated temperatures electromigration of donor defects in the semiconductor bulk. The drift of these ions changes with time the value of the electric field at the Au–CdTe interface and the value of resistance of the depletion region. The correlation between this field and the value of the reversed electric current is determined from the shape of current–voltage characteristics of the structure. We explain the change of the current with time as a result of changing electric field at the interface. The I_R-V measurement on the studied sample reveals that the field dependence of barrier height due to the image force is the mechanism responsible for the non-saturated reverse current. We also determined the initial value of the charge density and extracted the diffusion coefficients of the donor ions. The behavior of resistance of the depletion region with time confirms the proposed model of electromigration of positive ions under the field in the depletion region. The stability and possible recovery of the resistivity of the sample were checked out, and we note that there was only very weak tendency of the resistivity to revert to initial conditions even after 14 days.
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1. Introduction

Semiconductor electronic and optoelectronic devices with two electrode contacts are composed of a metal–semiconductor–metal (M–S–M) structure. The performance and the reliability of these devices are determined by charge carrier transport properties and charge collection efficiency, which are strongly influenced by the physical properties of the metal–semiconductor (M–S) interface.

The presence of mobile impurities in these semiconductor devices presents a technological problem. The migration of these impurities in the space charge regions disturbs the semiconductor's electrical properties [1,2]. One of the mechanisms, which cause degradation in the performance of these optoelectronic devices, is migration of impurities [3–7]. Understanding and control of migration of defects in semiconductors is of central importance for developing electronic and optoelectronic devices.

Cadmium telluride (CdTe) and cadmium zinc telluride (CZT) based materials are the materials of choice for room temperature X-ray and gamma ray detector applications. The group Ib elements Cu, Ag, and Au belong to the important impurities in CdTe compound. The mobility of these impurities in as-grown CdTe material disturbs self-compensation of charged defects in detector-grade material and locally changes the resistivity. Therefore, their control is considered as one of the key parameters in the production of CdTe for high-performance applications.

The diffusion of extrinsic Ag in CdTe was investigated using the radiotracer [8]. The origin of why Cu and Ag shows faster diffusion in CdTe than the other elements in group Ib was reported in Ref. [9], and *ab initio* investigation of the bulk diffusion profiles of Cd vacancy and other interstitials (Cu, Ag, Au and Mo) in CdTe was also recently reported [10]. CdZnTe is also used as a substrate for HgCdTe infrared detectors fabricated by MBE and LPE techniques. Impurities diffuse into the epilayer during epitaxial growth and deteriorate the quality of the final (HgCd)Te films [7].

To the best of our knowledge, there were no studies in pertinent literature about the influence of drift and diffusion of the intrinsic charged defects in external electric field (electromigration) on the transient current through M–S–M structure.

In this work, we developed a model to explain the current transients by electromigration of charged ion defects. The proposed model was applied to transient measurements performed on low-resistivity p-type CdTe with Au contacts and diffusion coefficients of ions were extracted.

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2. Theory

When gold and a p-type CdTe semiconductor (M–S) are brought together, electrons from the metal surface will flow to the semiconductor (the work function of metal $\varphi_M < \varphi_S$, the work function p-type of CdTe) and recombine with the holes within the layer of length L_d in the bulk. A negatively charged region is created near the semiconductor surface due to the ionized acceptor atoms. This charge creates a positive electric field and results in bending of the band edges of CdTe downwards (Fig. 1.).

Using the full depletion approximation the CdTe is depleted of mobile carriers within the depletion region of width L_d. The charge density ρ in that region is due to the difference between the ionized acceptors N_A and ionized donors N_D, the semiconductor is assumed neutral outside the depletion region. In this case, the spatial distribution of the potential function $\varnothing$ (x) and of the electric field $E(x) = -\frac{d\varnothing}{dx}$ can be found by solving the Poisson equation, which for the p-type semiconductor in one-dimensional case has the form [11]

$$\frac{d^2\varnothing(x)}{dx^2} = \frac{\rho}{\varepsilon\varepsilon_0} \tag{1}$$

$$\rho = q(N_A - N_D) \tag{2}$$

with boundary conditions that $\varnothing(0) = 0$ and $\varnothing(L_d) = V_d$. Here ε is the dielectric permittivity of the material (10.3 for CdTe), ε_0 is the vacuum permittivity and V_d $(=\varphi_M - \varphi_S)$ is the diffusion potential, $e\varphi_M$ and $e\varphi_S$ are the work functions for metal and p-type CdTe, respectively. This yields the following expressions for $E(x)$ and L_d [11]

$$E(x) = \frac{\rho}{\varepsilon\varepsilon_0}(L_d - x), \quad 0 \le x \le L_d \tag{3}$$

$$L_d(V) = \sqrt{\frac{2\varepsilon\varepsilon_0}{\rho}(V_d - V - kT/q)}. \tag{4}$$

where x is the distance from the interface of the Schottky contact, V is the external bias, k is the Boltzmann constant and T is the absolute temperature.

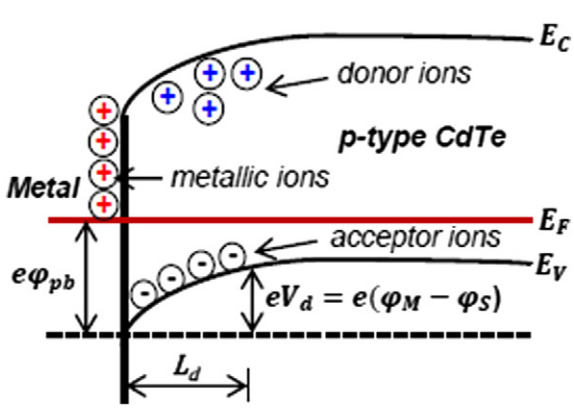

Fig. 1. Energy band diagram showing the bending of the bands near the M–S interface. $e\varphi_M$ and $e\varphi_S$ are the work functions for metal and p-type CdTe, respectively. $e\varphi_{pb}$ is the Schottky barrier height, V_d is the diffusion potential and L_d is the thickness of the depletion layer.

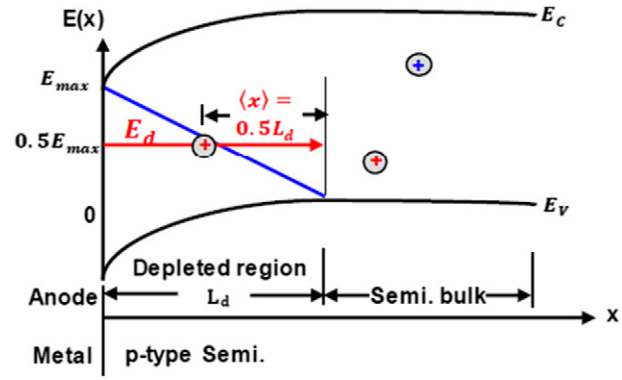

Fig. 2. Band diagram of a p-type semiconductor with Schottky contact showing the bending of the bands at the M–S interface under bias. The blue straight line denotes to profile of the electric field $E(x)$ in the depletion region of width L_d (Eq. (3)), which is assumed to cause electromigration of the charged defects that are elsewhere in the depletion region into the semiconductor bulk. The red line is the average electric field that has been used as a driving field E_d in the proposed model. The average distance traveled by the ions (x) is 0.5 L_d.

The electric field has linear profile in the depletion region (Fig. 2) with maximum value at the M–S interface. Using Eq. (4) in Eq. (3) and considering $V \gg V_d - kT/q$ the electric field profile is

$$E(x) = \sqrt{\frac{2\rho}{\varepsilon\varepsilon_0}V} - \frac{\rho}{\varepsilon\varepsilon_0}\,x. \tag{5}$$

2.1. Metal/p-type semiconductor/metal structure

M–S–M structure with two Schottky type contacts is formed when two metallic electrodes are connected to such a P-type semiconductor that the work function of the metal, $e\varphi_M$, is less than that for the p-type semiconductor,$e\varphi_S$. One of both Schottky contacts operates in reverse direction when the M–S–M is under bias. In case of low resistivity semiconductor material, almost all the bias is concentrated near the reverse biased contact of the structure, and the electric field is confined in the depletion region below this contact [12,13]. Therefore, the resistance of the structure is dominated by the resistance, R_R, of the depletion region.

The reverse current of an ideal Schottky contacts, according to the thermionic emission theory, should saturate at value I_0 that depends on the Schottky barrier height, φ_{pb}, and is independent of the applied voltage [11] as

$$I_0 = AA^*T^2 exp\left(-\frac{q\varphi_{pb}}{kT}\right). \tag{6}$$

where A^* is the Richardson constant; A is the area of the contact.

There are several causes of departure from this ideal behavior [14]. Tunneling current through the barrier is dominating and the transport mechanism is thermionic field emission when the energy parameter $E_{00} = qh/4\pi\left(\frac{N}{m^*\varepsilon\varepsilon_s}\right)^{0.5}$ is in the order of kT [15]. This requires carrier concentration $N \approx 3 \times 10^{19}$ cm^{-3} at 400 K (in case of CdTe material with effective mass of holes $m^* = 0.8m_0$, here m_0 is the electron rest mass). Such a carrier concentration is several orders of magnitude higher than for standard undoped and compensated semiconductors [16–18].

There are two different mechanisms reported as a reason that the reverse current does not saturate at high temperatures and low doped semiconductors [11,19].

The first mechanism is the field dependence of barrier height. The barrier height φ_{pb}, is a decreasing function of the electric field strength E_0 at the M–S interface. In this case the reverse current is given as

$$I_R = I_0 exp\left(\frac{q\Delta\varphi_b}{kT}\right) \tag{7}$$

where $\Delta\varphi_b$ is the barrier lowering due to the field. The simplest form of barrier lowering is due to the image force (Schottky effect), and it given by [11]

$$q\Delta\varphi_b = \sqrt{\frac{qE_0}{4\pi\varepsilon\varepsilon_0}}. \tag{8}$$

The other mechanism that has been reported as a reason that I_R does not saturate and depends on the bias is the assumption of standard diffusion model of contacts [19], in which the electric field at the M–S interface E_0 is properly correlated to the reverse current, I_R, as

$$I_R = Aq\mu_h p_0 E_0 \tag{9}$$

where, the free carrier density, p_0, is given by Schottky barrier, φ_{pb}, that is independent of the bias, μ_h is constant hole mobility.

We can determine from the I–V measurement which of the both mechanisms is dominating. From Eq. (5) follows

$$E_0 = \left(\frac{2\rho}{\varepsilon\varepsilon_0}\right)^{1/2} V^{1/2}. \tag{10}$$

Using Eqs. (10), (8) in Eq. (7) and Eq. (10) in Eq. (9) we note that both mechanisms expect non-linear I–V characteristics. However, for the first mechanism (barrier lowering), a straight line between $\ln(I)$ and $V^{1/4}$ is expected, while the diffusion model mechanism expects a straight line relationship between I and $V^{1/2}$. Therefore the dominating effect can be determined from the I–V measurements. In both cases, the current increase with time is a consequence of the increase of the electric field E_0 at the M–S interface.

One of the reasons for increase of E_0 and I_R with time is the detrapping of charge carriers from deep level (polarization phenomena) [20,21]. However, the characteristic time of this process τ ($= (N_V\sigma\nu)^{-1}exp(E_T/kT)$) is 1.7 s at 300 K and 5.6×10^{-4} s at 400 K in case of high resistivity CdTe material (N_V is density of states at the valence band edge, v is hole thermal velocity, and the deep level is at energy $E_T = 0.75$ eV with capture cross section; $\sigma = 10^{-14}$ cm^2). Furthermore, the Fermi level, and then the trap level, is located close to the valence band in the low resistivity p-CdTe material, therefore, the polarization phenomena appear faster than that of high resistivity material.

In some cases, the transient current shows high value of characteristic time, in hours scale at high temperature. The interpretation of such long characteristic time of the transient current remains unclear.

2.2. Model

We assume that the high electric field confined in the depletion region causes at higher temperatures electromigration of the donor defects from the depletion region into the semiconductor bulk. The drift of these positive ions increases the charge density ρ with time and decreases the resistance, R_R of the depletion region. Consequently the electric filed E_0 and the transient I_R will increase with time.

To estimate the characteristic time for the electromigration process we apply a simple model introducing an average value of the electric field across the depletion region (the driving field E_d). From Eq. (3) follows

$$E_{max} = E(0)_{max} = \frac{\rho_{max}}{\varepsilon\varepsilon_0} L_{dmi}. \tag{11}$$

where L_{dmi} is value of L_d at ρ_{max}. From Eq. (2), the max. charge density is qN_A, and by assuming that $L_{dmi} \approx L_d$. Therefore the driving field is

$$E_d = \frac{E_{max}}{2} = \frac{qN_A}{2\varepsilon\varepsilon_0} L_d. \tag{12}$$

The assumption that $L_{dmi} \approx L_d$ has little effect on estimated parameters. For example, in case of the charge density increases one half of its value (i.e. $\rho_{max}/\rho = 3/2$), therefore, from Eq. (4), $L_{dmi}/L_d \approx 0.82$, which increases E_d by factor 1.2 of its value. This error affects only the diffusion coefficient that will be determined from the Eq. (14) below, however, the other quantities estimated in Section 4.2 are not subjected to this error.

Assuming that x is the average distance traveled by the donor ions to the edge of the depletion region in time τ, then

$$\langle x \rangle = v_d\tau = \mu E_d \tau \tag{13}$$

here v_d and μ are the drift velocity and mobility of the ion respectively. The average distance crossed by the ion to leave the depletion region is $L_d/2$ (Fig. 2.) Using the Nernst–Einstein equation $\mu = qD/kT$ and inserting Eq. (11) in Eq. (12) we obtain

$$\tau = \frac{\varepsilon\varepsilon_0 kT}{q^2 N_A D}. \tag{14}$$

where D is the diffusion coefficient of donor ions. In case of presence of several types of positive ions with different ion motilities the transient current due to the ion drift can be written as

$$I_R(t) = a + \sum_i b_i exp\left(-\frac{t}{\tau_i}\right). \tag{15}$$

here a and b_i are time independent constants.

The proposed model is based on the M–S–M structure of Schottky barrier type contacts. The applicability of the model is limited to those structures of low resistivity semiconductor material and to higher temperatures. In such configuration, high electric field is confined in the depletion region below the reverse biased contact, Fig. 2. which supposed to cause electromigration of the ions from depletion region to the semiconductor bulk.

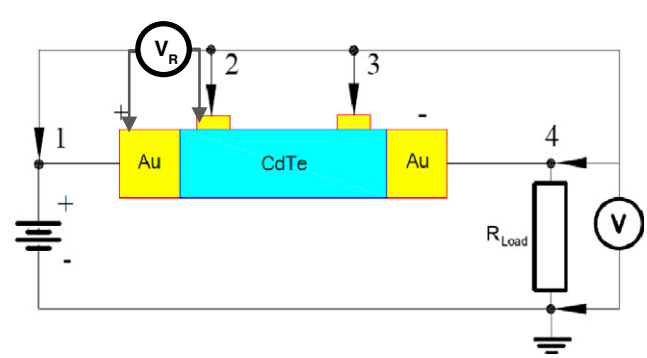

Fig. 3. Schematic diagram of sample configuration used for electromigration measurement.

3. Material and experimental technique

The sample studied in this work is a non-intentionally doped low resistivity p-type CdTe prepared in the Institute of Physics of Charles University in Prague by the Bridgman method from Te-rich melt. It has a rectangular bar shape with dimensions $1.6 \times 2 \times 10$ mm^3.

We obtained the experimental results of I–V characteristics using the four probe method (Fig. 3). Four Au contacts were deposited on the sample by evaporation and Ag wires were soldered on the contact using silver paste. The sides of the sample were optically polished with final 0.05 mm grit and chemically etched in 1% Br-methanol solution for 1 min. Two current contacts were located at the ends of the bar (No.1, 4). Two potential probes (No. 2, 3) were placed approximately 1.5 mm from the current contacts.

The I–V characteristic was measured at 402 K. The voltage was measured across contacts No. 1 and 4, and the current I was measured by measuring the voltage V across a reference series load resistor, R_{Load}, as $I = V/R_{Load}$.

The variation of the resistance of the depletion region R_R was measured by soldering two additional Ag wires to the contacts No. 1 and 2 (Fig. 3) and monitoring the voltage drop V_R between them with time. We calculated the resistance R_R as V_R/I. Here I is the current passing through the sample.

Furthermore, the sample configuration in Fig. 3 allows measuring the voltage drop across the bulk semiconductor part (V_{23}) and bias V_{34} between contacts 3 and 4.

4. Results and discussions

4.1. I–V characteristic

Fig. 4 shows the I–V characteristic of the studied sample at 402 K. We can see that the characteristic is almost symmetrical and non-linear type, which indicates that both contacts are Schottky type contacts [15]. The relation between $\ln(I)$ and $V^{1/4}$ in the $V > 5V$ range (to fulfill the condition that $V \gg V_d - kT/q$) is presented in Fig. 5. The data are very well fitted to a straight line indicating that the barrier lowering by the image force effect, Eqs. (7) and (8), is the dominating mechanism responsible for the fact that I_R does not saturate and depends on the bias. Furthermore, inserting Eqs (10) and (8) in Eq. (7) we obtain the slope of the straight line $\left(q^2\rho/8\pi^2\varepsilon^3\varepsilon_0{}^3\right)^{1/4}/kT$. From the values of the slopes of the two lines in Fig. 5, we estimate the average density of the charge carriers at 402 as $\rho/q = (N_A - N_D) \approx 3 \times 10^{15}$ cm^{-3}, which agrees well with the concentration of residual acceptors typical for CdTe material [*e.g.* 22].

The intercepts of the straight lines in Fig. 4 equal the values of $\ln(I_0)$ at the measuring temperature (Eq. (7)). The average value of I_0 (*at* 402*K*) obtained from Fig. 5 is $240x10^{-6}$ *A*, Using this value in Eq. (6)

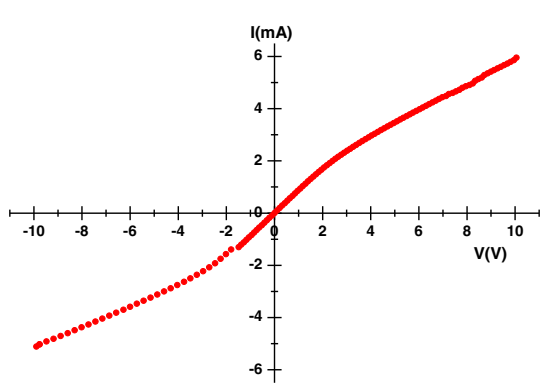

Fig. 4. I–V characteristic of the studied sample at 402 K.

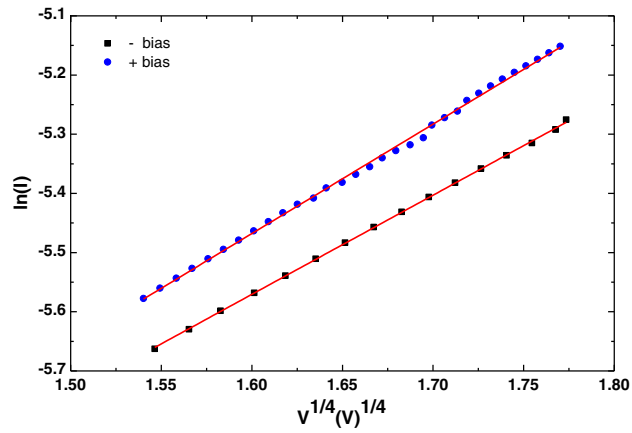

Fig. 5. *ln(I) versus* $V^{1/4}$ plots. Symbols represent experimental data from Fig. 4 and solid lines represent the fitted straight line.

the zero-field Schottky barrier height is extracted as $q\varphi_{pb} \approx 0.71$ eV (the contact area $A = 2 \times 1.6$ mm^2 and the Richardson constant for p type CdTe $A^* = 42$ A cm$^{-2}K^{-2}$ [23]). From the data in Ref.[23] one can expect the value of barrier height of the n-type CdTe/Au $T = 129$ °C around 0.78 eV. Adding this value for n-type to our value 0.71 eV retrieved for p-type CdTe, we obtain the value of 1.49 eV at 402 K. This fits with the reported value of CdTe bandgap [24,25] at this temperature.

4.2. Evaluation of E_d, N_A and N_D at Au/p-type CdTe interface

The transient current I_R of the studied sample at 402 K and 5 V is presented in Fig. 6. As expected from the proposed model, the current increase with time is observed. We can see that I_R is increased by 2.5 times of its initial value in time $t = 4.2 \times 10^3$ s. Using the value of the residual acceptor density calculated from the I–V characteristic ($\approx 3 \times 10^{15}$ cm^{-3}) in Eq. (10) the initial value of the electric field at M–S interface results is $E_{0i} = 7.9 \times 10^6$ V/m. The increment of the electric field at the M–S interface necessary to increase I_R (by 2.5 times) is estimated from Eq. (8) and Eq. (7) as 1.84 times of its initial value E_{0i}. This means that the maximum electric field at the M–S interface (after time t from application of the bias) is $E_{max} \cong 1.4x10^7$ V/m. Then the driving electric field E_d is 7×10^6 V/m.

We suppose that the ions will leave the depletion region under the effect of E_d, and then the charge density would increase with time to its maximum value ρ_{max} at E_{max}. The value of $\rho_{max}(\cong qN_A)$ is determined from Eq. (10), thus, the value of N_A is estimated as $N_A \cong 9.3 \times 10^{15}$ cm^3.

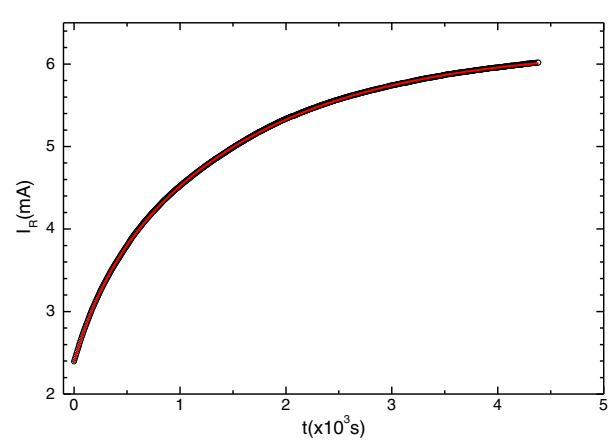

Fig. 6. Measured current transients at 402 K and 5 V. Exponential fit to the data are also shown as red solid line.

Therefore, the density of the donor is estimated as $N_D = N_A - 3 \times 10^{15} \cong 6.3 \times 10^{15}\ \mathrm{cm}^{-3}$, which agrees with the typical donor density in undoped CdTe material [*e.g.* 25,26].

4.3. Transient current measurements and estimation of the ion diffusion coefficient

The data of the transient current of the studied sample show excellent double exponential fit and yield two characteristic times, 269.5 s and 1546 s (Fig. 6). We attribute these time constants to the drift of two positive ions from the depletion region to the semiconductor bulk. By using the estimated value of $N_A = 9.3 \times 10^{15}\ \mathrm{cm}^{-3}$ in Eq. (14), the diffusion coefficients are evaluated as $1.4 \times 10^{-14}\ \mathrm{cm}^2/\mathrm{s}$, and $8 \times 10^{-14}\ \mathrm{cm}^2/\mathrm{s}$. These values fit well with the diffusion coefficients of mobile impurities (Li, Cu, Na, K, Ag) in CdTe with similar carrier concentration determined by Lyubomirsky [27] using the transient ion drift method [28]. The results also are in agreement with that reported in [29, 30]. It was found that the application of low bias (1 V) at a temperature of 150 °C resulted in Cu migration and the formation/dissociation of (Cu_{Cd}–V_{Cd}) A-centers in CdTe/CdS structure [29], and at room temperature. There was no electromigration of Ag ions in p-CdTe [30].

We expect that the diffusion coefficient of Au, D_{Au}, in CdTe is much less than the values of D that have been determined here. The extrapolation of high-temperature experimental data [31] to 402 K yield $D_{Au} = 6 \times 10^{-24}\ \mathrm{cm}^2/\mathrm{s}$. Furthermore, the diffusion of ions from electrode needs higher temperatures, in Au–Si appears at 370 °C [14]. We thus deduce that Au (neither from electrode nor defects in the depletion region) is not the diffusing species in our model.

The interface (surface) states are typically connected with multiple type lattice imperfections formed mostly by native defects, dislocations and their conglomerates. In p-CdTe the most important relatively mobile defects are negatively charged Cd vacancies with estimated diffusion coefficient similar to that evaluated in the manuscript. However, the diffusion of negatively charged Cd vacancies would result in an opposite resistivity behavior than observed in our experiment. We thus deduce that Cd vacancies may be neglected.

4.4. Depletion region resistance measurements

The proposed model predicts the reduction of the resistance of the depletion region as a result of electromigration of the ions to the semiconductor bulk part of the sample. The departures of these positive ions increase the charge density in the depletion region and consequently increase the electric field and hence reduce the resistance, R_R, of this region. Fig. 7 presents such measurement, in which R_R is decreasing with time. The behavior of R_R with time confirms the proposed model of electromigration of positive ions under the field in the depletion region.

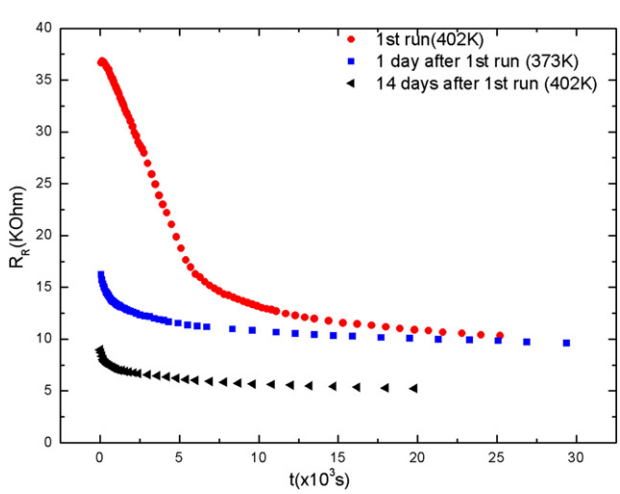

Fig. 7. Time dependence of the resistance of the depletion region.

The values of the voltage drop across the rest of the sample (V_{23} and V_{34}) was also monitored with time, we note that they are almost unchanged, probably because the migrated ions spread out in large volume of the sample.

Belas et al. [32] studied the electromigration of the charged defects in an undoped CdTe sample, but in the semiconductor bulk of the sample (away from the depletion region). A bias between two electrodes probe along the sample was applied at 100 °C and a change with time of the resistance between probes was also obtained indicating of electromigration of ions. They also confirmed the electromigration of the ions by measuring PL spectra [32].

With the aim to check the stability and possible recovery of the resistivity to initial value we have performed follow-up relaxation experiments — 1 day after the 1st relaxation run at 373 K and 14 days after the 1st relaxation run at 402 K. The sample was stored at room temperature between relaxations. The data shown in Fig. 7 prove that there is only very weak tendency of the resistivity to revert to initial conditions even after 14 days. We have also stored the sample at 402 K without biasing four hours and identified only negligible changes of the resistivity.

5. Conclusion

We proposed a new model to interpret the transient current in metal–semiconductor–metal structure with two Schottky contacts fabricated to low resistivity p-CdTe material. We identified the electromigration of the donor ions in the depletion region formed at the reverse biased M–S interface as the responsible mechanism for the transient current flowing through the structure. We applied the proposed model to the $I_R(t)$ measured on low-resistivity p-type CdTe with Au contacts and identified the correlation between the electric field at the M–S interface and I_R from I–V characteristic as the field dependence of barrier height due to the image force. We determined the density of the residual acceptor and the zero-field Schottky barrier height at 402 K from the I–V measurements of the studied sample. We also extracted the acceptor density, the donor density and the diffusion coefficients of two donor ions using the proposed model. Their values fit well with that published about the same material, but measured by different techniques. We observed a reduction in the value of the resistance of the depletion region with time, which confirms the proposed model of electromigration of positive ions under the field in the depletion region. We carried out follow-up relaxation experiments to check recovery of sample resistivity. We found out that there was only very weak tendency of the resistivity to revert to initial conditions even after 14 days.

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