Time Relaxation of Point Defects in p- and n-(HgCd)Te after Ion Milling

E. BELAS,[1,5] V.V. BOGOBOYASHCHYY,[2] R. GRILL,[1] I.I. IZHNIN,[3] A.P. VLASOV,[4] and V.A. YUDENKOV[3]

1.—Institute of Physics, Charles University, Prague 2, CZ-121 16, Czech Republic. 2.—Kremenchuk State Polytechnical University, 39614 Kremenchuk, Ukraine. 3.—R&D Institute for Materials SRC "Carat," 79031 Lviv, Ukraine. 4.—Lviv National University, 79044 Lviv, Ukraine. 5.—E-mail: belas@karlov.mff.cuni.cz

Time relaxation of the electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) of the n-type layer created by ion milling is investigated in Hg vacancy-doped, As-doped, and In-predoped p-type, and In-doped n-type $Hg_{1-x}Cd_xTe$ ($0.2 < x < 0.22$) samples. We show that the n-type layer is formed, and the temperature-activated relaxation occurs in all cases. The annealing at 75°C results in a gradual degradation of the converted n-type layer and a back n-to-p conversion within 8 days. The existence of a high-conducting, surface-damaged region with a high-electron density ($\sim 10^{18}$ cm^{-3}) and a low mobility ($\sim 10^3$ cm^2/Vs) is confirmed, and its influence on the relaxation is studied.

Key words: (HgCd)Te, type conversion, ion milling

INTRODUCTION

Narrow-gap $Hg_{1-x}Cd_xTe$ is a well-known material for fabrication of long-wavelength and mid-wavelength infrared detectors. Most of the detectors are of the photovoltaic type, and the p-n junction is usually formed by ion implantation or diffusion. In the last few years, a new method for the preparation of the p-n junction was developed based on dry etching (DE) (ion milling (IM) or reactive ion-plasma etching (RIE)) of as-grown p-type material. It was found that DE results in the conversion of undoped p-type (HgCd)Te ($x \approx 0.21$) to n-type over a large depth (≈ 100 μm) within a short time (≈ 10 min) at room temperature.[1–4] The p-to-n conversion was also observed in As-doped, p-(HgCd)Te both at RIE[5] and IM.[6] There is a general agreement in recent papers that the type conversion occurs because of the creation of Hg interstitials (Hg_I) (donor) at the surface during DE and their fast diffusion into the sample,[1–7] where they fill Hg vacancies (V_{Hg}) (acceptor) or form complexes with foreign acceptors.[8,9] Very good quality p-n junctions were produced by DE, and high-performance, IR photovoltaic detectors were fabricated as well.[10–13] Up to now, the time stability of these structures was presented only in Ref. 8, where the time relaxation of the electrical conductivity σ(77 K) in Hg vacancy-doped, p-(HgCd)Te after DE was reported to be $\sim 10^3$ times longer than the etching time. The theoretical model of the relaxation based on the capture of Hg_I on defects inside the sample during DE and their successive liberation was proposed.[8]

The list of observed effects connected with the type conversion of p-(HgCd)Te was given in Ref. 8. The dominant discussion is held now about three special topics. (1) The diffusion model results in the square-root etching-time, t, dependence of the thickness of the converted layer, d.[2] There are, however, indications, that such a dependence is not true in some cases, and $d \propto t^\alpha$ with $0.5 < \alpha < 1$ is reported.[1,13] For an explanation of this dependence, the simple theoretical model based on a gradual formation and saturation of the Hg_I surface source was developed.[14] (2) The formation of a surface-damage region during DE with the thickness of a few microns, a low mobility, and a high-electron density in comparison to the converted bulk n-type layer is observed.[3,15,17] The nature and effect of such a layer to the n-type formation has not been thoroughly studied yet. (3) The stability of the DE that created the n-type layer has become a substantial question since the thermally activated time relaxation of the layer has been found.[8]

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Table I. Initial Parameters of Investigated Samples

$Hg_{1-x}Cd_xTe$	Hg Vacancy-Doped P1; P2	As-Doped	In-Predoped	In-Doped N1, N2
Type	p	p	p	n
Thickness (μm)	938; 907	97	935	1056
Conductivity ($\Omega^{-1}cm^{-1}$)	0.5	0.8	0.7*	7
Concentration (cm^{-3})	7×10^{15}	3×10^{16}	6×10^{15}*	2×10^{14}
Hall mobility ($cm^2V^{-1}s^{-1}$)	700	240	670	210,000

*The initial n-type conductivity and electron density were 82 Ω^{-1} cm^{-1} and 3×10^{15} cm^{-3}, respectively.

In this paper, the time relaxation of σ(77 K) and Hall coefficient R_H(77 K) of $Hg_{1-x}Cd_xTe$ ($0.2 < x < 0.22$) samples with both p- and n-type conductivity after IM is studied in more detail. Simultaneously, the effect of the surface-damaged region on the relaxation is investigated.

EXPERIMENT

The vacancy-doped p-type and In-doped n-type $Hg_{1-x}Cd_xTe$ ($0.2 < x < 0.21$) bulk-single crystals were prepared by a modified, vertical-directed crystallization method in Svetlovodsk, Ukraine. The As-autodoped, p-type (HgCd)Te, variable-bandgap epitaxial layers ($x \approx 0.22$) were grown by a evaporation-condensation-diffusion method in Lviv National University. The initial thickness and electrical properties of the investigated samples are given in Table I. The In-predoped p-(HgCd)Te was prepared by annealing of the In-doped, n-type crystal under a near-saturated Hg overpressure at a temperature of 395°C, which resulted in the creation of V_{Hg} and the n-to-p conversion. An IB-3 ion-beam etching system (EIKO, Japan) with Ar^+ ions was used for ion milling. The energy of the Ar ions was 500 eV, current density 100–200 μA/cm^2, and milling time 600–1,200 sec. The time relaxation of σ(77 K) and R_H(77 K) at two different magnetic fields (0.05T, 1T) were measured on square-shaped samples in the Van der Pauw configuration, where about a 2-μm layer of the milled surface was removed on some samples by chemical etching next to IM. Afterward, IM samples were kept in open air at alternatively 20 ± 2°C (room temperature), 50°C, and 75°C between particular measuring steps. The temperature changes (20°C, 50°C, or 75°C ↔ 77 K) took less than 1 min to avoid indeterminate periods. The thickness of the converted layer in the As-autodoped sample was found to be d = 10 μm by the differential Hall-effect measurement. In the other p-type samples, the etching conditions were set so that d ≈ 30–40 μm.

RESULTS

Figure 1 shows the time relaxation of σ(77 K) and R_H(77 K) of the n-type converted layer created by IM in vacancy-doped p-(HgCd)Te from which ≈2 μm of the milled surface was removed after IM (sample P1). We see that the relaxation occurs during the whole presented time interval (300 days), and the conductivity can be well approximated by the trial function:

$$\sigma(77\ K)(\Omega^{-1}cm^{-1}) = 1.03 - 0.2 \log t\ (day) \quad (1)$$

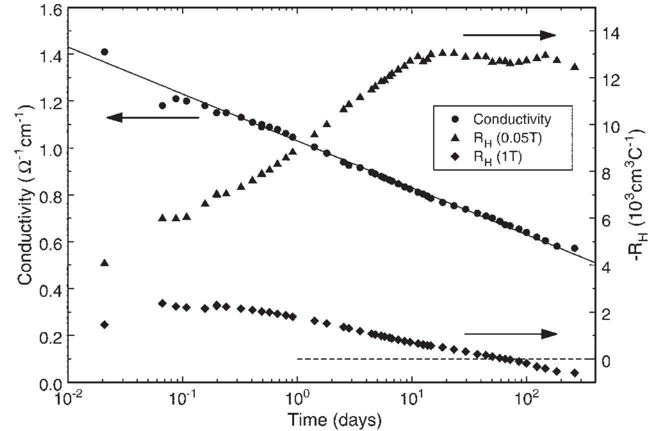

Fig. 1. The time dependence of the integral electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) at two magnetic fields (0.05T; 1T) of the n-type layer created by IM in vacancy-doped, p-(HgCd)Te (P1) where 2 μm of the milled surface was removed immediately after IM. The sample was stored at room temperature between measurements. The conductivity is fitted by σ(77 K) = 1.03 − 0.2 log t.

Measurements on this sample continue to find the final steady state of the sample.

The temperature-accelerated time relaxation of σ(77 K) and R_H(77 K) of the milled sample was investigated in vacancy-doped p-(HgCd)Te (sample P2, the same material as P1), where the milled surface was not etched. The results are shown in Fig. 2. The small increase of measured values 160 h after IM was caused by unintentional short overheating of the sample during the heating from 77 K to room temperature.

The time relaxation of σ(77 K) and R_H(77 K) of the In-doped n-(HgCd)Te (sample N1) modified by IM, where ≈2 μm of the milled surface was removed, is plotted in Fig. 3. This relaxation is faster than in the vacancy-doped, p-type sample and completely stops after 2 weeks. An accelerated relaxation was also observed at 50°C and 75°C.

The n-type layer was formed by IM in As-doped and In-predoped p-(HgCd)Te as well. The milled surface of these samples was not etched. The results of the time relaxation of σ(77 K) and R_H(77 K) of this layer are presented in Figs. 4 and 5.

The detailed comparison of the room-temperature relaxation of vacancy-doped p-type (P1, P2) and

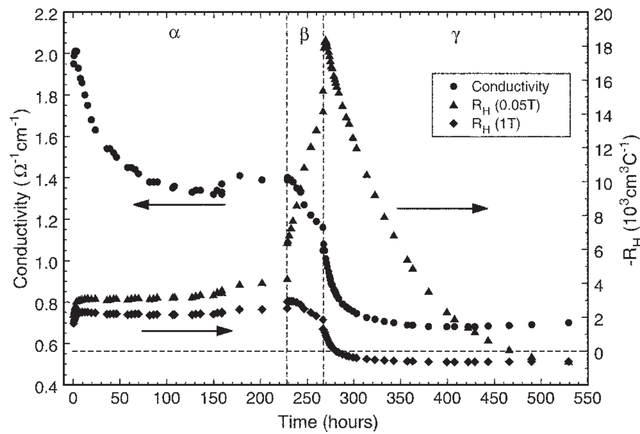

Fig. 2. The time dependence of the integral electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) at two magnetic fields (0.05T; 1T) of the n-type layer created by IM in vacancy-doped, p-type (HgCd)Te (P2), where the milled surface was not removed. The sample was stored at room temperature (part α), at 50°C (part β), and at 75°C (part γ) between measurements. The dashed labels separate the regimes.

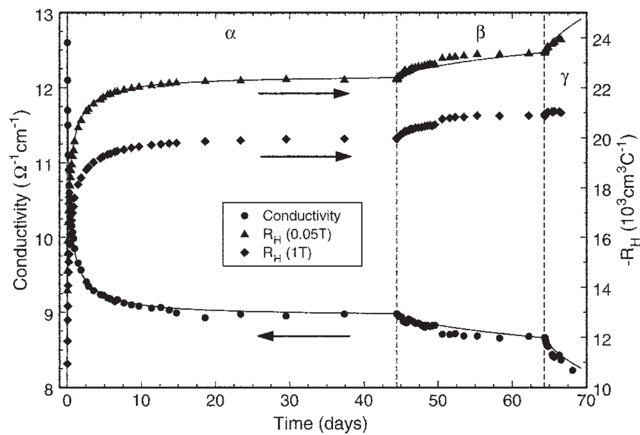

Fig. 3. The time dependence of the integral electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) at two magnetic fields (0.05T; 1T) of IM modified n-type layer in In-doped, n-type (HgCd)Te (N1), where 2 μm of the milled surface was removed immediately after IM. The sample was stored at room temperature (part α), at 50°C (part β), and at 75°C (part γ) between measurements. The dashed labels separate the thermal regimes. Full lines show the fit within the trap model.[8]

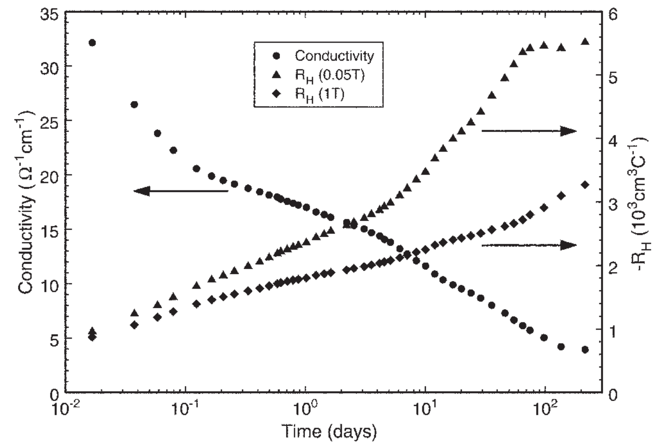

Fig. 4. The time dependence of the integral electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) at two magnetic fields (0.05T; 1T) of the n-type layer created by IM in As-doped, p-type (HgCd)Te, where the milled-surface layer was not etched. The sample was stored at room temperature between measurements.

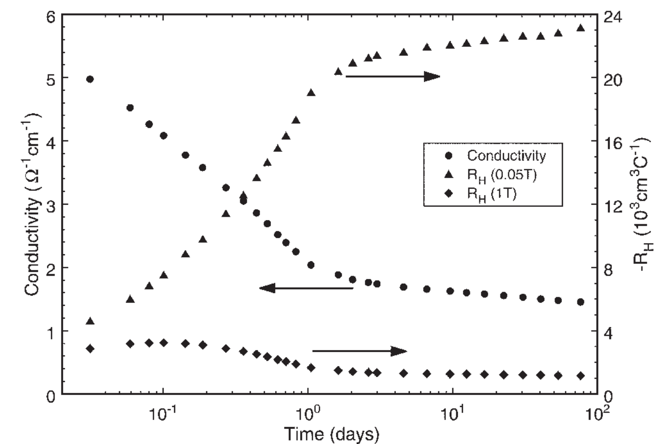

Fig. 5. The time dependence of the integral electrical conductivity σ(77 K) and Hall coefficient R_H(77 K) at two magnetic fields (0.05T; 1T) of the n-type layer created by IM in In-predoped, annealed p-type (HgCd)Te, where the milled-surface layer was not etched. The sample was stored at room temperature between measurements.

In-doped n-type (N1, N2) samples, with ≈2-μm etched/unetched of the damaged layer removed from the milled surface by the chemical etching immediately after IM is shown in Fig. 6. We observe that the conductivity of the vacancy-doped, p-type sample with an unetched-damaged layer increases and reaches the maximum 2 h after IM. This specific effect (reproduced twice in two different samples) did not appear in other samples, where σ(77 K) decreases immediately after milling. This dual evolution cannot be explained by the delay caused by the chemical etching, which took a few minutes only. The list of galvanomagnetic relaxation data of all samples is given in Table II.

DISCUSSION

The analysis of the electron mobility, μ_e, and density of the whole milled n-type layer consisting of the

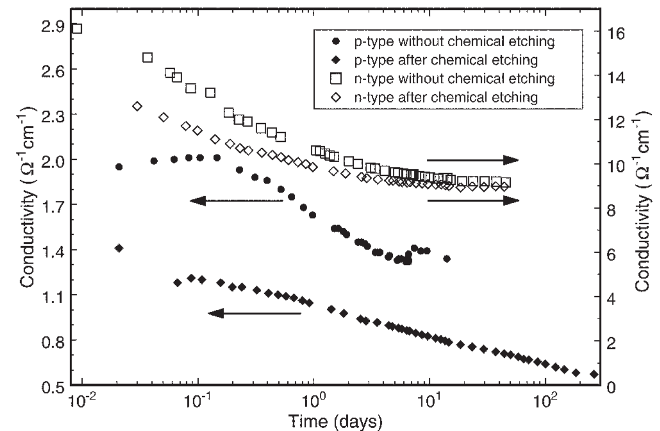

Fig. 6. The integral electrical conductivity σ(77 K) versus time of undoped p-type (P1, P2) and In-doped n-type (N1, N2) samples with removed/unremoved 2 μm of the milled surface.

Table II. Integral Galvanomagnetic Properties of Investigated Samples after 40 Min, 5 Days, and Long-Time Relaxation after Ion Milling at Room Temperature

Time	Parameters	Hg Vacancy-Doped P1; P2	As-Doped	In-Predoped	In-Doped N1; N2
40 min	σ (Ω^{-1}cm^{-1})	1.4; 2	28	5	12.6; 15
	$-R_H$(0.05T) (cm^{3}C^{-1})	4,100; 2,200	1,160	4,600	13,900; 9,400
	$-R_H$(1T) (cm^{3}C^{-1})	1,460; 1,640	1,000	2,870	10,950; 6,800
	μ_e (10^3 cm^2/Vs)	8.7; 5.8	33	27	175; 141
5 days	σ (Ω^{-1}cm^{-1})	0.885; 1.34	13.9	1.68	9.2; 9.6
	$-R_H$(0.05T) (cm^{3}C^{-1})	11,700; 3,200	2,980	21,700	21,700; 20,000
	$-R_H$(1T) (cm^{3}C^{-1})	1,010; 2,150	2,070	1,300	19,300; 15,700
	μ_e (10^3 cm^2/Vs)	23; 6.7	44	61	200; 192
Long	σ (Ω^{-1}cm^{-1})	0.57; (#)	4	1.45	(#); 9.2
	$-R_H$(0.05T) (cm^{3}C^{-1})	12,500; (#)	5,500	23,100	(#); 21,500
	$-R_H$(1T) (cm^{3}C^{-1})	−600; (#)	3,300	1,160	(#); 18,700
	μ_e (10^3 cm^2/Vs)	44; (#)	27	62	(#); 200

(#) The samples were annealed at higher temperature, and the room-temperature data are not available.

surface-damaged layer and the bulk-converted layer is difficult because of the unknown properties of the damaged layer. Assuming identical initial samples P1 and P2, where the difference in the treatment is only the chemical etching of 2 μm of the surface layer from sample P1, the comparison of the P1/P2-transport data elicited shortly after IM yields the surface-electron mobility $\mu_e^s = 1{,}300$ cm^2/Vs and the density $n_e^s = 1.4 \times 10^{18}$ cm^{-3}, which corresponds to the conductivity in this layer, 280 Ω^{-1}cm^{-1}. These values, especially the extremely low μ_e^s being about 9× less than the mobility observed at such doping density in non-compensated (HgCd)Te,[16] point to enormous damage of the surface layer. Such a damaged layer was also reported in Ref. 17, where the low μ_e was detected by the quantitative mobility-spectrum analysis.

The low μ_e was not confirmed in Ref. 8, where the fit, assuming a high μ_e of ~10^5 cm^2/Vs within the whole n-type, was possible. In addition, much faster relaxation and a deeper p-n junction were reported there. We judge that the effect of the damaged layer was suppressed there by a much higher thickness of the converted-bulk, n-type layer relatively to the thickness of the damaged layer and by sputtering of the surface (a few microns), which removed a significant part of the damaged layer. It is also possible that the surface of the sample was slightly overheated because of the higher current density (600 μA/cm^2) of the Ar atoms used in the etching experiments,[8] which probably resulted in accelerated relaxation and a higher thickness of the converted n-type layer.

The effect of the damaged layer also limits the effective electron mobility in the converted layer. To evaluate the experimental data, we have also included in Table II average electron mobility in the converted layer calculated via approximate formula

$$\mu_e = \frac{|R_H|\sigma^2}{\sigma - \left(1 - \frac{d}{L}\right)\sigma_p} \quad (2)$$

which is valid far from the inversion of R_H in a weak magnetic field, $R_H \equiv R_H(77\ K)$ at 0.05T and $\sigma \equiv \sigma(77\ K)$. The symbols σ_p, d, and L are the conductivity of the initial p-type at 77 K, the thickness of the converted layer, and the thickness of the sample, respectively. The electron mobility in n-type samples N1 and N2 was obtained simply as $\mu_e = |R_H\sigma|$.

We see in Table II that the time relaxation results in a partial recovery of the damaged layer, but the high final μ_e of ≈10^5 cm^2/Vs typically reported for the n-type converted layer[3,15] is not reached except for the n-type samples N1 and N2. The recovery is also supported by the measurements of R_H(77 K) in higher magnetic field 1T. The divergence of R_H(1T) from R_H(0.05T) during the relaxation proves the increasing effect of electrons with higher mobility to the transport data.

The complete theoretical description of the relaxation of the whole n-type layer is complicated because of an unknown mechanism of the damaged-layer evolution. It could relax via recombination of defects in the layer without significant interaction with the rest of the converted n-type. It can, however, also serve as a source of additional Hg_I to sustain the propagation of the converted layer similarly as it was reported for ion-implanted (HgCd)Te.[18] The latter eventuality is probably responsible for the smooth increase of σ(77 K) shortly after IM in the case of sample P2 in Fig. 6. The theoretical model of the relaxation suggested in Ref. 8 did not take the damaged layer into account and could not be applied on p-type samples here. In the case of the In-doped n-(HgCd)Te samples, the effect of the damaged layer to the relaxation is damped, and the model[8] can be applied, as shown in the fit in Fig. 3. There is an open question at this moment: is the relaxation an exclusive characteristic feature of the damaged layer or is there also active relaxation of the converted n-type far from the surface? The problem can be solved by the measurement of the relaxation of the pure-converted n-type layer created by IM with removal of the whole damaged-surface layer.

The set of experiments at higher temperatures demonstrates the thermal activation of the relaxation.

The relaxation at 50°C can be recommended to accelerate the process significantly without apparent effect to the stability of the relaxed n-type layer. The higher temperature, about 75°C, is inappropriate because of the gradual degradation of the converted n-type layer and the reverse n-to-p conversion within ~200 h.

The standard diffusion model describing the propagation of p-n junction in p-(HgCd)Te caused by dry etching, which gives the square-root time dependence of the thickness of the converted region, assumes the steady state of the surface source and constant-surface Hg_I concentration. The formation of the damaged layer violates such an assumption. The gradual saturation of the surface source until the defect production and annihilation in the damaged region reaches the dynamical equilibrium results in a more linear course,[14] exactly as it is reported in the literature.[1,13]

CONCLUSIONS

The detailed investigation of the time relaxation of σ(77 K) and R_H(77 K) of the n-type layer created by IM in p- and n-type (HgCd)Te ($0.2 < x < 0.22$) samples was presented. It was found that the relaxation is a general feature after IM observed in Hg vacancy-doped, As-doped, and In-predoped p-type and In-doped, n-type samples. In some cases, the visible long-time relaxation proceeds for 1 year. In addition, it was observed that the relaxation is a thermally accelerated process, which practically does not take place at 77 K. The n-type layer created by IM is destroyed if the sample is annealed at 75°C for ~8 days.

The long-time relaxation of the electrical properties of the n-type layer created by IM in both p- and n-type (HgCd)Te is a very important effect that must be taken into account in the production of the time-stable (HgCd)Te photodiodes fabricated by dry etching. The presence of a surface-damaged layer and the gradual change of the electric properties in optoelectronic devices could disturb their operation.

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