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Long-term stability of electron concentration in HgCdTe-based *p–n* junctions fabricated with ion etching

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HIGHLIGHTS

- Long-term (over 10^6 min) stability of HgCdTe-based *p–n* junctions fabricated with ion etching was studied.
- The stability was shown to depend on the growth technique, substrates and doping.
- Indium doping is shown to be a solution for the problem of instability of electron concentration where appropriate.

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ABSTRACT

Results of experimental studies of long-term (~7 years) stability of electron concentration in HgCdTe-based *p–n* junctions fabricated with ion etching (IE) are presented. The stability was studied during the storage of ion-etched samples at the room temperature with periodical measurements of carrier concentration and mobility with the use of the Hall effect. It is shown that after $\sim 10^3$ min after IE electron concentration in un-doped HgCdTe films grown by molecular-beam epitaxy (MBE) on GaAs substrates stabilizes at $\sim 10^{15}$ cm^{-3} and does not change in 7 years of storage of the films. In contrast to that, in films grown by liquid phase epitaxy and by MBE on Si substrates, electron concentration continues to decrease during all the period of storage and gets lower than 10^{14} cm^{-3}. For such films, donor doping of the material is recommended, which for indium doping with concentration from 10^{15} to 10^{16} cm^{-3} is shown to be able to keep stable electron concentration for all the studied period of time. In bulk HgCdTe crystal doped with silver, fast re-conversion of the *n*-region of a *p–n* junction fabricated with IE back to *p*-type was observed. The results obtained show some limitations of IE in relation to fabrication of *p–n* junctions for HgCdTe-based photodetectors, and suggest how these limitations can be avoided.

1. Introduction

Mercury cadmium telluride (MCT) solid solutions remain to be the basic materials for fabricating multi-element infrared (IR, wavelengths 2–20 μm) photodetectors with ultimate parameters. This status of MCT is due to the specific electronic structure of this material and is expected to remain as such for at least two decades more [1,2].

One of the methods of fabricating *p–n* junctions required in MCT-based photodiodes is ion or plasma etching of the material with initial *p*-type conductivity conditioned by vacancy or extrinsic acceptor doping [3–8]. The method is based on a specific interaction of low-energy (100–1000 eV) ions (typically, Ar^+) or plasma with MCT surface. This interaction results in formation of n^+–*n*–*p* or n^+–*n* structure [9] with radiation-damaged surface n^+-layer (with the thickness of 1–3 μm) and the 'main' *n*-layer. The thickness of the latter depends on the parameters of the initial material

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and these of ion treatment (with ion and plasma etching producing very similar effects) and may achieve hundreds of micrometers. Right near the surface, the n^+-layer has high electron concentration n_{77} (up to 10^{18} cm^{-3}) and low electron mobility μ_{n77} ($\sim 10^4$ cm^2/(V s)) (as measured at 77 K for MCT with composition $x \sim 0.2$), and n_{77} decreases and μ_{n77} increases from the surface into the bulk of the material. The 'main' n-layer has uniform values of n_{77} and μ_{n77} throughout its thickness, and these values correspond to high-quality material with very low electrical compensation. It is these values that eventually define the parameters of a photodetector, and in most cases (at least, for the un-doped material) they are determined by background donors, whose typical concentration in high-grade MCT is believed to be about 10^{15} cm^{-3} [9]. This value is just what is required for many types of photodetectors, so it is often a custom to rely on the concentration of background donors N_{BD} for fabricating, for example, n-regions in IR photodiodes made with ion/plasma etching [3–8]. In such diodes, concentration p_{77} and mobility μ_{p77} of the holes in the part of the sample, which was not affected by the etching, remain equal to those of the initial material. It was shown that during ion/plasma etching, in the subsurface MCT layer forms a source of non-equilibrium interstitial mercury atoms (Hg_I) with very high concentration ($\sim 10^{14}$ cm^{-3} in contrast to the equilibrium value of $\sim 10^6$ cm^{-3}) [9–12]. This predefines very quick movement of the diffusion front of Hg_I and complete annihilation of mercury vacancies (which means conductivity type conversion in p-type material and modification (decrease in electrical compensation level) in n-type material). If the treated material contains extrinsic acceptor dopants (such as As, Sb, Cu, Ag or Au), Hg_I forms donor centers or complexes with these atoms [10–13]. As early as at the advent of ion/plasma etching p–n junction MCT technology, it was established [14,15], that when the process of the etching ended, a pronounced relaxation of electrical parameters of the converted (modified) layer proceeded during 10^3–10^5 min of the storage of the etched samples at the room temperature (let us call such relaxation a short-term one). This fact was confirmed by the results of numerous studies performed on various MCT samples [16–20]. The relaxation is due to disintegration of donor complexes, which were formed by the interstitial mercury with uncontrolled or intentionally introduced acceptors and tellurium nanocomplexes (if any) because of the fast decrease of Hg_I concentration, and is expressed in decrease of electron concentration and increase in electron mobility. (Reasons for the absence of full re-conversion of conductivity type at the room temperature back into p-type, however, remained unclear, as was the exact mechanism of the disintegration of the donor complexes). Generally, it is believed that after the relaxation the electron concentration in the n-region of a p–n junction fabricated with ion/plasma etching is defined by N_{BD} and thus, should be stable [9,16–20]. However, it appeared that relaxation not always ended after 10^5 min of storage [16,17], also, up to now it has not been clear whether the constant level of n_{77} seemingly achieved during 10^5 min of aging should pertain over longer storage time. A preliminary study on the stability of MCT-based IR photodetectors fabricated with the use of ion etching (IE) [18] resulted only in a qualitative conclusion that the n^+–n structure formed with the etching remained as such after 10 years of storage at the room temperature. Considering the importance of the stability of the parameters of photodiodes designed with achieving and maintaining ultimate IR detection parameters in view, we followed quantitative parameters of n-type structures fabricated with the use of IE during a long (>10^6 min, about 7 years) period of storage. The obtained data also proved to be important in establishing the mechanism of the disintegration of donor complexes in ion-etched MCT doped with arsenic, and for assessing the eligibility of IE as a tool for establishing N_{BD} after the short-term post-etching relaxation.

2. Experimental

Studied were MCT films grown by molecular-beam epitaxy (MBE) on GaAs, Si and CdZnTe substrates (including films doped with donors (In) or acceptors (As)), films grown by liquid-phase epitaxy (LPE) on CdZnTe substrates and a sample of bulk MCT crystal doped with Ag (an acceptor). The electrical properties of the films were investigated by measuring the Hall coefficient R_H and conductivity σ in the magnetic field B of 0.01 up to 1.5 T at $T = 77$ K. The measurements were performed on square-shaped van der Pauw structures. The $R_H(B)$ and $\sigma(B)$ dependences were analyzed using Discrete Mobility Spectrum Analysis (DMSA) [10]. In samples subjected to IE, the use of DMSA allows for considering the contribution of the ion-damaged n^+-surface layer, and to study defects in the n-type 'bulk' of the treated sample, thus revealing the material properties in question [10–12,16–20].

IE was performed using an IB-3 (EIKO, Japan) etching system with Ar^+ ion energy of 500 eV, a current density of 0.1–0.2 mA/cm^2, and an etching time of 20 min. The temperature of the sample holder during the etching was kept at ~293 K by means of cooling the holder with water. Post-etching relaxation was studied by aging samples in air at 293 ± 2 K.

3. Results

3.1. Un-doped films and films doped with In, grown by MBE on GaAs ($x \sim 0.2$)

The data on short-term relaxation in samples considered in this section were reported on in Ref. [19]. These were samples M10 (un-doped) and M11, M12 and M14, doped with In (donor) with concentrations N_{In} from 10^{14} up to 10^{16} cm^{-3}, designated as samples ##1–4 in Ref. [19], respectively. In addition to these samples, we now also studied relaxation in specimen M10p which was a piece of sample M10 subjected to 2nd IE after the short-time relaxation. Parameters of the initial (before IE) samples are given in Table 1.

Relaxation curves for electron concentration and mobility of the studied samples after IE are given in Fig. 1. As can be seen in this figure, after the period of short-term relaxation, which in this case lasted up to 3×10^4 min, both electron concentration and mobility levelled off and hardly changed during the next few years of storage.

As mentioned above and discussed in Ref. [19], after the relaxation electron concentration $n_{77}(f)$ in un-doped samples should equal to N_{BD}, thus for samples intentionally doped with indium with N_{In} we get $n_{77}(f) = N_{In} + N_{BD}$. In un-doped film M10 and in film M11 with $N_{In} = 3 \times 10^{14}$ cm^{-3} the value of n_{77} leveled off at $\sim 2 \times 10^{15}$ cm^{-3}. In this case, indium doping appeared to be of little use, as N_{BD} was greater than N_{In}. In films M12 and M14, $n_{77}(f) = N_{In} + N_{BD}$. Also, in samples M10 and M11 the electron concentration in as-grown films appeared to be much lower than $n_{77}(f)$ value, which spoke of high electrical compensation in the films before the etching, and confirmed the fact that the etching eliminated compensation. Therefore, in these films $n_{77}(f)$ truly reflected the N_{BD} value. This was also confirmed by the result obtained during the 2nd IE of M10 film, namely, on sample M10p. As can be seen in Fig. 1, relaxation curve for electron concentration in this film after 2000 min of aging repeated that of sample M10 after the 1st IE. The difference in electron concentration after the 1st and the 2nd IEs at the first stage of relaxation (~1000 min) was due to the specifics of donor complexes, which Hg_I atoms form with tellurium-related defects in MBE MCT, and has no relation to residual donors [20].