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TELLURIUM EFFECT ON DEGRADATION STABILITY OF SEMIINSULATING GALLIUM ARSENIDE CRYSTALS

Initial untreated crystals of semiinsulating tellurium-compensated GaAs are shown to degrade considerably less after HF treatments in comparison with the corresponding specimens doped with chrome, which testifies to a substantial influence of the compensating impurity type on the substance degradation stability. Semiinsulating tellurium-compensated GaAs crystals preliminary treated in hydrogen plasma are also found to have higher degradation stability with respect to the action of long-term high-frequency and microwave treatments in comparison with raw crystals.

K e y w o r d s: degradation stability of crystals, Czochralski technique, internal mechanical stresses.

1. Introduction

In works [1, 2], it was shown that the degradation stability of chrome-compensated semiinsulating GaAs crystals to the influence of a high-frequency electromagnetic field and thermal treatments can be improved by treating the specimens in hydrogen plasma. In this work, we studied the influence of the tellurium impurity on the properties of semiinsulating gallium arsenide (SIGA) crystals grown up by the Czochralski technique. Certainly, a change of the atomic number of a doping element and, hence, the covalent radius of an atom will affect the processes of emergence and relaxation of internal mechanical stresses (IMSs) in SIGA. This assumption is confirmed, in particular, by the results obtained in work [3], where epitaxial GaAs structures on the Sn- or Te-doped (100) GaAs substrate were studied. The authors of work [3] established that those structures bend substantially, if a film 20–60 μm in thickness is doped with silicon, and the bending results from the presence of IMSs in the film. However, if, in the course of film growing, tin was introduced into the solution-melt in a concentration of 4 wt.%, the bending disappeared. This fact testifies to the practical absence of IMSs in this structure. In this case, silicon precipitates in the film disappeared, and the dislocation density decreased by two orders of magnitude, which testified to a substantial influence of the IMS level on the structural perfection and the properties of GaAs. This relation was emphasized many times earlier [1, 2, 4]. It also confirms the influence of the doping impurity type on the characteristics concerned. In this connection, this work was aimed at researching the influence of the tellurium impurity on the properties of SIGA crystals. A special attention is focused on the study of the degradation stability of both raw SIGA specimens and SIGA crystals preliminary treated with plasma to the action of high-frequency (HF) and microwave (MW) treatments.

2. Experiment

Tellurium-doped SIGA crystals with the (100) orientation grown up, by using the Czochralski technique, are studied. The specific resistance of specimens amounted to $1 \times 10^7\ \Omega \cdot$ cm. Some of the specimens were first treated in hydrogen plasma on a PE-CVD installation, by following the technique described in works [1, 2]. Then the specimens were subjected to the HF-treatment at a frequency of 13.56 MHz (on the same installation) and to the microwave treatment (MWT) at a frequency of 2.45 GHz. For the MWT, we used an installation on the basis of a magnetron with a specific output power of

Parameters of the fitting of the Raman spectra of GaAs specimens by Gaussians

Specimen of GaAs	Band area, rel. units	Position of band maximum, cm^{-1}	Band half-width, cm^{-1}	Impurity
Raw	13715.15	293.10	6.1032	Te
Specimen No. 4	48556.00	293.46	6.2389	Te
Specimen No. 1	47831.85	293.61	6.7867	Te
Raw	1808.10	292.64	4.1073	Cr [2]
After hydrogen plasma treatment	1635.40	291.62	4.4308	Cr [2]

N o t e. In an unstressed GaAs crystal, the band of LO-phonon Raman scattering is observed at 291.3 cm^{-1} [7].

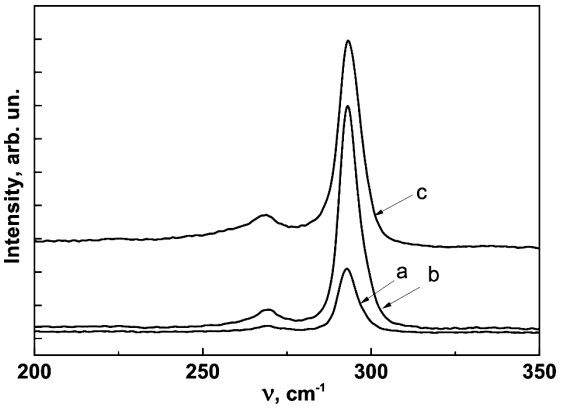

Fig. 1. Raman spectra of GaAs specimens: raw (a), No. 1 (b), and No. 4 (c). See Table for the specimen nomenclature

1.5 W/cm^2. The MWT was carried out in the working chamber of a magnetron in air in a free space.

Besides raw SIGA, specimens Nos. 1 and 4 were examined, which underwent the following treatments. Specimen 1: the treatment in hydrogen plasma for 30 min, the subsequent two-stage HF treatment with a total duration of 119 min, and then the stage-by-stage MWT with a total duration of 10 min. Specimen 4: the two-stage HF treatment with a total duration of 119 min and the stage-by-stage MWT with a total duration of 10 min.

IR transmission and reflection spectra were measured on a Fourier-spectrometer Infralum FT-801 in a spectral interval of 4–16 μm at room temperature. Raman scattering spectra were measured using the exciting radiation from an argon laser with the wavelength $\lambda = 488$ nm at room temperature.

3. Results and Discussion

The replacement of the compensating ^{24}Cr impurity by the ^{52}Te one with covalent radii of 118 and 136 pm, respectively, should affect the kinetics of IMS level change in SIGA crystals. In Fig. 1, the Raman spectra of Te-doped SIGA crystals are shown, and Table presents the results of their fitting by Gaussians. As was mentioned above, a change of the doping impurity type should substantially affect the stability of a SIGA crystal with respect to further treatments that are capable of changing the IMS level in it and, accordingly, the defect subsystem state. It is worth to note that the stresses in raw Te-doped SIGA crystals are larger than in Cr-doped ones, but the degree of their relaxation at treatments is lower. The former fact follows from a comparison of the energies of LO phonons for raw SIGA specimens doped with chromium (292.64 cm^{-1} [2]) and tellurium (293.10 cm^{-1}, Table 1) and those for an unstressed GaAs crystal (291.3 cm^{-1} [5]). The latter conclusion is confirmed by the results obtained for the treated specimens. Really, from Fig. 1 and Table, one can see that the band in the Raman spectrum of SIGA doped with tellurium, which is responsible for the scattering by a LO phonon, becomes insignificantly shifted even after multistage treatments (see specimens 1 and 4 in Table). At the same time, even a short plasma treatment of SIGA doped with Cr induces a considerable variation in the LO-phonon peak position and, hence, the IMS relaxation (Table).

It is evident that considerable stresses in SIGA can result in the appearance of many structural defects in the material, e.g., dislocations. Really, as is seen from Table, the half-width of the LO phonon band in the Raman spectrum of a specimen doped with tellurium ($\Delta\omega = 6.1032$ cm^{-1}) is much larger than that in the case of a chrome-doped specimen ($\Delta\omega = 4.1073$ cm^{-1}).

In Fig. 2, the transmission and reflection spectra in the IR spectral range of the SIGA crystal doped

with Te after a number of active treatments are depicted. First, the crystal was subjected to the HF treatment under a mask, in the plasma discharge mode, and in two stages: for 62 and 57 min. As is seen from Fig. 2, after the first HF treatment, the transmittance of the crystal decreased by about 1.5% in the whole examined spectral interval (Fig. 2, spectrum 4-2t). It is important to mark that the reflectance did not change: neither after the first stage of the HF treatment nor after the second one. This fact means that all variations of the transmittance are associated with changes in the bulk properties of the crystal as a result of IMS relaxation processes in it under the influence of treatments.

It should be noted that the second HF treatment even enhanced the crystal transmittance to some extent (Fig. 2, spectrum 4-3t). At the same time, all the next treatments (MWTs at a frequency of 2.45 GHz) led only to a worse crystal transmittance. One can see that the MWT with a total duration of 10 min resulted in a substantial decrease of the crystal transmittance in the whole examined spectral interval (Fig. 2, spectrum 4-7t). As was shown in work [6], the MWT is a powerful method, which allows the crystal to be heated up at an extremely high temperature rate. Therefore, in our opinion, the transmittance drop is also related to the MWT-induced heating of the crystal and a partial relaxation of IMSs in it by means of the generation of additional structural defects.

However, since the properties of the raw Te-doped GaAs crystal differ from those of Cr-doped GaAs [2], the transmittance reduction as a result of the IMS relaxation is substantially different. Really, as is seen from Fig. 2, the transmittances of raw SIGA doped with Te decreased after the HF treatment only by about 1.5%, whereas that of SIGA doped with Cr by about 6% (Fig. 3, spectrum 3 [2]). In work [2], it was shown that a quick thermal annealing of Cr-compensated SIGA gives rise to a catastrophic degradation of the crystal (Fig. 3, spectrum 4 [2]). At the same time, one can see from Fig. 2 that the MWT of the Te-compensated specimen for 10 min decreased its transmittance only by about 3% (Fig. 2, spectrum 4-7t). Moreover, even the long-term (for 30 min) thermal annealing of Te-doped SIGA at 550 °C did not result in such a catastrophic drop of the transmittance (the corresponding spectra are not presented) as the quick thermal annealing of Cr-compensated SIGA.

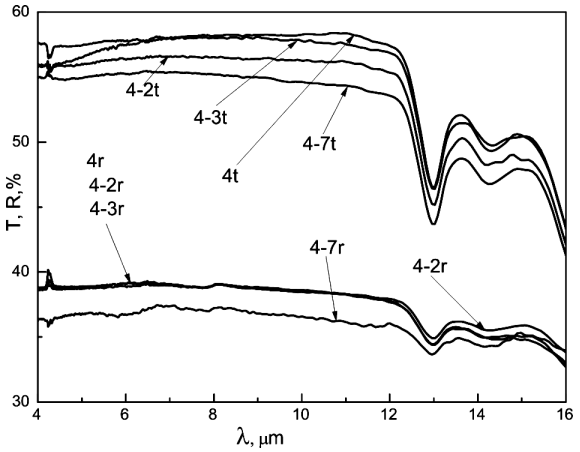

Fig. 2. IR transmission (t) and reflection (r) spectra of tellurium-doped GaAs specimens: (4) raw specimen, (4-2) specimen 4 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 62 min), (4-3) specimen 4-2 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 57 min, (4-7) specimen 4-3 after the microwave treatment for 10 min

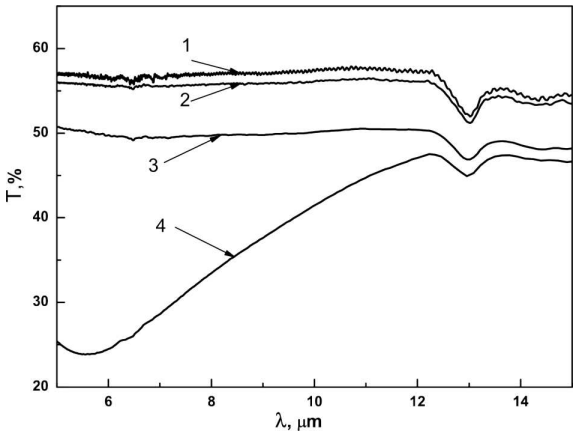

Fig. 3. IR transmission spectra of Cr-doped GaAs specimens [2]: (*1*) raw specimen, (*2*) specimen 1 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 15 min), (*3*) specimen 2 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 47 min, (*4*) specimen 3 after the annealing at 600 °C for 30 min in the argon atmosphere

It is also worth to note that the reflectance of a SIGA crystal changes only after a long-term (for 10 min) MWT (Fig. 2, spectrum 4-7r). In our opinion, this circumstance may be related to the fact that

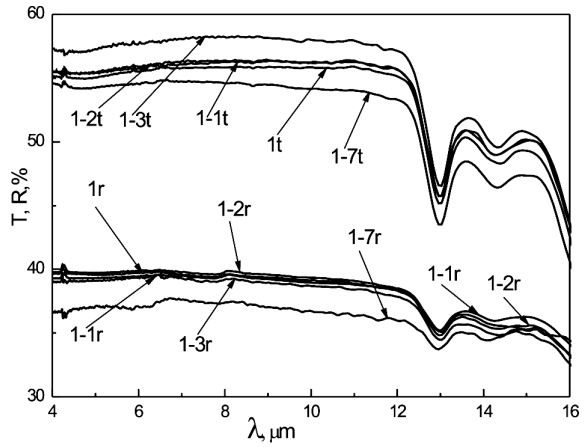

Fig. 4. IR transmission (t) and reflection (r) spectra of GaAs specimens: (1) raw specimen, (1-1) specimen 1 after the treatment in H^+ plasma (a discharge power of 175 W, a gas pressure of 0.8 Torr, a treatment time of 30 min), (1-2) specimen 1-1 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 62 min, (1-3) specimen 1-2 after the HF treatment under a mask (a discharge power of 250 W, a gas pressure of 0.8 Torr, a treatment time of 57 min, (1-7) specimen 1-3 after the microwave treatment for 10 min

this is a time interval of MWT needed for the crystal to be heated to temperatures, at which films of other phases, e.g., GaN [7], can be formed on its surface. As a result, the structure reflectance can decrease, owing to the reasons described in work [7]. The atmosphere was a source of nitrogen required for the formation of GaN, because the MWT were carried out in air.

The treatment of Te-doped SIGA crystals in hydrogen plasma did not worsen their transmittance, but, on the contrary, even enhanced it to some extent (Fig. 4, spectrum 1-1t). This fact was associated with changes of the properties in the near-surface region of the crystal rather than on its surface. This conclusion is confirmed by the fact that the reflectance practically did not change after the plasma treatment (Fig. 4, spectra 1r and 1-1r). In addition, it was also found that the surface structuring of specimens owing to the plasma treatment, which could result in a reflectance reduction, also did not occur. From the atomic force microscopy researches, it was found that the average surface roughness even decreased from 1.567 to 1.090 nm after the treatment.

After the first stage of the HF treatment, the transmittance of the plasma-treated crystal did not worsen (Fig. 4, spectrum 1-2t), unlike the raw specimen (Fig. 2, spectrum 4-2t). The second stage of the HF treatment even enhanced the transmittance in the whole spectral range (Fig. 4, spectrum 1-3t). This means that we observe once more the improvement of the degradation stability of the crystal following the mechanism that is similar to one proposed in works [2, 7] for SIGA doped with chrome. According to this mechanism, the defects generated in the crystal bulk during the HF treatment can move toward the surfaces under the influence of the mechanical stress gradient and annihilate in the plasma-treated near-surface layer with defects available there. Only the long-term MWT worsened the SIGA transmittance (Fig. 4, spectrum 1-7t). In this case, the variation dynamics of reflectance spectra (Fig. 4, spectra 1r to 1-7r) is analogous to the variation of spectra for the specimen not subjected to the plasma treatment (Fig. 2). It should be noted that the absolute value of transmittance drop for the plasma-treated specimen after the long-term MWT (about 1.2%) is smaller than that for the raw one (about 3%). This fact also testifies that the plasma treatment makes it possible to improve the degradation stability of SIGA crystals with respect to the influence of the combined HF + MW treatment.

4. Conclusions

Summarizing the results obtained, the following conclusions can be drawn. The introduction of an impurity with a larger covalent radius into SIGA improves the degradation stability of the latter with respect to the influence of further technological treatments. This effect is observed for both initial (raw) crystals and crystals treated in hydrogen plasma. The mechanism of degradation stability enhancement in the plasma-treated SIGA crystals does not depend on the type of a doping impurity.

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ВПЛИВ ТЕЛУРУ
НА ДЕГРАДАЦІЙНУ СТІЙКІСТЬ КРИСТАЛІВ
НАПІВІЗОЛЮЮЧОГО АРСЕНІДУ ГАЛІЮ

Р е з ю м е

Показано, що вихідні, необроблені кристали напівізолюючого GaAs, компенсовані телуром, після ВЧ-обробок деградують істотно менше порівняно зі зразками, легованими хромом. Даний ефект свідчить про суттєвий вплив типу компенсуючої домішки на деградаційну стійкість матеріалу. Також встановлено, що кристали напівізолюючого GaAs, компенсовані телуром, що пройшли попередню обробку в плазмі водню, мають вищу деградаційну стійкість до впливу тривалих високочастотних і мікрохвильових обробок, порівняно з необробленими кристалами.