Neutron transmutation doping of III–VI layered semiconductors

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Results on neutron transmutation doping of III–VI layered semiconductors (GaS, GaSe, InSe) are reported. The evolution of electrical and optical properties before and after thermal annealing shows that neutron induced defects are recombined at temperatures of 400°C for InSe, 470°C for GaSe, and 520°C for GaS. The resistivity of the annealed samples is about five orders of magnitude lower than that of as irradiated materials. Optical absorption tails and peaks in the forbidden band, appearing in as irradiated samples, disappear after annealing and the shape of the intrinsic absorption edge is recovered. MST/3283

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Introduction

Neutron transmutation doping (NTD) is a highly reproducible method for semiconductor doping and it is particularly applicable where it is desired to control the uniformity of doping.[1,2] The method involves the irradiation of a semiconductor with thermal neutrons. The isotopes of the host lattice atoms capture neutrons, depending on their relative abundance and capture cross-section, and transmute, through different nuclear reactions, to stable species that can act as doping agents.

Since Koma *et al.*[3] proposed the so called Van der Waals epitaxy, III–VI layered semiconductors have received renewed interest. Epitaxial growth of GaSe on InSe and InSe on GaSe has been already carried out.[4] The possibility of epitaxial growth between layered materials has been demonstrated even with lattice mismatch up to 50%.[5] In this context, the problem of doping becomes crucial. Recently, successful n-doping of InSe by the NTD method has been obtained for concentrations up to 10^{17} cm^{-3} (Ref. 6). As grown GaSe is p type with very low hole concentrations and GaS is semi-insulating. Attempts to obtain n type materials by conventional doping methods have not been successful.[7] In this work the possibility of n doping these semiconductors by NTD is tested and the results of the annealing process of irradiation induced lattice damage are reported.

Experimental

Starting materials of InSe, GaSe, and GaS were grown by the Bridgman method. For each material, samples about 1 mm in thickness and 5×10 mm^2 in area, were extracted from the same ingot and exposed to a flux of thermal neutrons of $4{\cdot}4 \times 10^{11}$ cm^{-2} for 253 h for GaS and GaSe and 380 h for InSe, corresponding to fluences of 4×10^{17} and 6×10^{17} cm^{-2}, respectively. The fast neutron flux on the samples was lower than 5% of the thermal neutron flux and the samples remained at room temperature.

The main impurities introduced by NTD are Sn in InSe and Ge in GaSe and GaS, according to the following nuclear reactions

$$^{115}\mathrm{In}\ (\mathrm{n}, \gamma)\ ^{116}\mathrm{In} \rightarrow\ ^{116}\mathrm{Sn}\ (\beta^- \text{ decay})$$

$$^{69}\mathrm{Ga}\ (\mathrm{n}, \gamma)\ ^{70}\mathrm{Ga} \rightarrow\ ^{70}\mathrm{Ge}\ (\beta^- \text{ decay})$$

$$^{71}\mathrm{Ga}\ (\mathrm{n}, \gamma)\ ^{72}\mathrm{Ga} \rightarrow\ ^{72}\mathrm{Ge}\ (\beta^- \text{ decay})$$

Another impurity, As is also introduced through the transmutation of Se via the reaction

$$^{74}\mathrm{Se}\ (\mathrm{n}, \gamma)\ ^{75}\mathrm{Se} \rightarrow\ ^{75}\mathrm{As}\ (\text{electronic capture})$$

In InSe the contribution of the last reaction only represents 0·26% of all nuclear reactions, while in GaSe it represents 14%, which would, in principle, produce compensation.

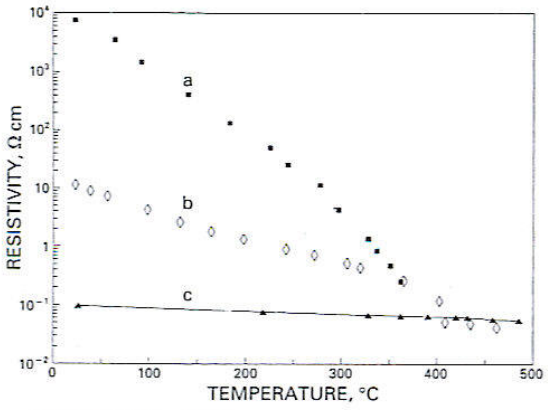
The resistivity and Hall measurements were performed using the Van der Pauw configuration on square samples of area about 5×5 mm^2 and thicknesses varying from 10 to 40 μm obtained by thinning of the irradiated samples. Ohmic contacts were made by thermal evaporation in vacuum of In in the case of InSe and Ag for GaSe and GaS. The optical absorption spectra were recorded in an optical system including a 25 cm focal length monochromator and synchronous detection. The annealing treatments were carried out in vacuum to avoid surface oxidation. Isochronal annealing steps of about 10 min were performed on all the samples.

Results and discussion

ELECTRICAL MEASUREMENTS

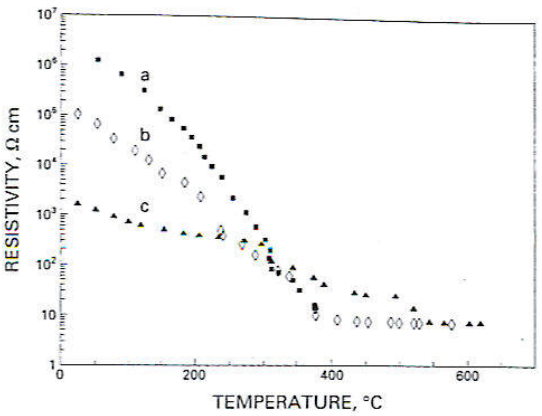
After irradiation at the specified doses, the resistivity of the InSe and GaSe increases by four and two orders of magnitude, respectively, with respect to the starting material. In GaS, a lower resistivity is observed after irradiation. In both cases, the recoil of the γ rays and β^- particles and the action of fast neutrons produce a high concentration of point defects. At room temperature the compounds GaSe and InSe contain free carrier concentrations of the order of 10^{15} cm^{-3}. After irradiation, free carriers can be trapped by the defects and their mobility is also expected to be reduced by lattice disorder, so an increase of resistivity is to be expected, as is observed. In contrast, the GaS starting material was semi-insulating and the high concentration of induced defects decreases the resistivity owing to the presence of a low concentration of free carriers from ionisation of defects, or to hopping conduction processes.

Lattice damage can be removed by thermal annealing. Figures 1, 2, and 3 show the change in resistivity during successive annealings for InSe, GaSe, and GaS respectively. In InSe (Fig. 1), the first annealing performed isochronally up to 360°C causes a monotonic decrease of the resistivity, which increases again when the sample returns to room temperature (RT). After a second isochronal annealing up to 460°C the electrical resistivity still decreases and remains



a 360°C; *b* 460°C; *c* 480°C

1 Resistivity of InSe irradiated with a thermal neutron fluence of 6×10^{17} n cm^{-2} for successive annealing treatments at given temperatures



a 370°C; *b* 570°C; *c* 620°C

3 Resistivity of GaS irradiated with a thermal neutron fluence of 4×10^{17} n cm^{-2} for successive annealing treatments at given temperatures

nearly constant on returning to RT. This is the expected behaviour in Sn doped InSe[8] and confirms that Sn atoms from transmuted In are in substitutional sites and act as completely ionised shallow donors at room temperature.

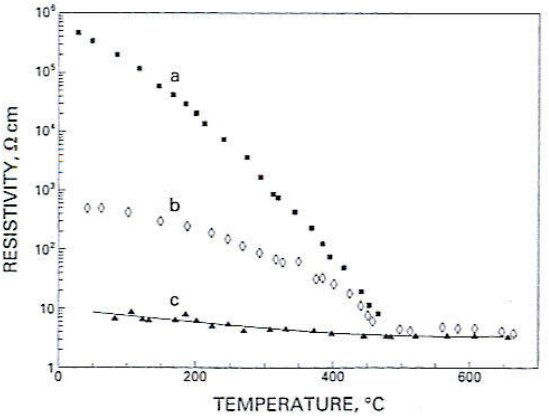
In GaSe (Fig. 2), a similar behaviour is observed, with a total decrease of resistivity by five orders of magnitude, but a higher temperature (500°C) is necessary to produce a completely irreversible resistivity decrease. In GaS (Fig. 3) the resistivity decrease after annealing is smaller and resistivity is always temperature dependent, in spite of the higher annealing temperatures. The reduction in resistivity suggests the existence of some type of doping effect. Unfortunately, any comparison with conventionally Ge doped GaS and GaSe is not possible, owing to the lack of published results.

OPTICAL MEASUREMENTS

Figure 4 shows the absorption coefficient for irradiated samples of the three compounds, before and after annealing. A modification of the absorption edge is observed in the as irradiated materials. In InSe, this modification appears simply as a broadening of the fundamental absorption step. In GaSe, a new absorption tail is observed below the exciton peak. In GaS, a series of absorption peaks with Gaussian shape are apparent, with energies of 1·52, 1·89, and 2·3 eV, below the indirect absorption edge. A resonant absorption peak above the band gap at energy 2·6 eV is also observed.

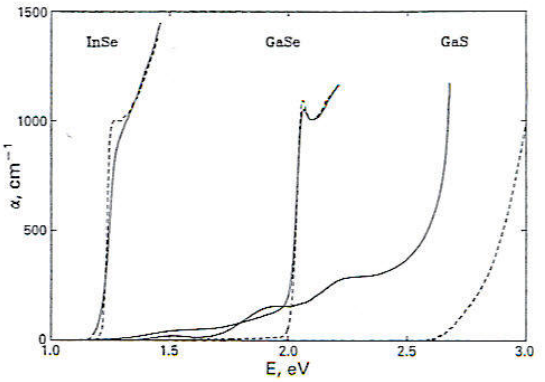
After annealing at 450°C the shape of the intrinsic absorption edge is recovered in InSe and GaSe. At this temperature, defect absorption peaks are still observable in GaS. As with the transport results, a higher annealing temperature (550°C) is necessary in GaS, in order to recover the intrinsic optical absorption edge.

Irradiation defects are likely to be Frenkel pairs formed by a vacancy (originated by the recoil of the γ or β^- particle emission), and an interstitial Sn or Ge atom. Positron annihilation spectroscopy confirms the presence of a high concentration of vacancy-like defects, through the increase of positron lifetime in the as irradiated samples.[9] Concerning optical properties, these defects would, in principle, behave as complex centres, giving rise to Gaussian shaped absorption peaks. These are actually observed in GaS, but not in GaSe or InSe. The fact that absorption peaks in the bandgap are observed only in the semiconductor with the highest energy gap (GaS) may be understood by assuming that in the lower gap semiconductors (GaSe and InSe) the optical transition energies in these centres are of the same order as those in GaS and then, being resonant with more intense intrinsic band to band transitions, they can not be observed. In GaSe, only the low energy tail of defect related optical transitions is observed. In InSe the effect of



a 460°C; *b*, *c* 660°C

2 Resistivity of GaSe irradiated with a thermal neutron fluence of 4×10^{17} n cm^{-2} for successive annealing treatments at given temperatures



4 Absorption coefficients for layered semiconductors InSe, GaSe, and GaS before (broken lines) and after thermal annealing (continuous lines)

irradiation defects only appears through the reduction of the exciton lifetime, due to the lattice disorder, giving rise to a broadening of the absorption edge.

This model is in agreement with the behaviour of optical properties after annealing. The recombination of Frenkel pairs gives rise to a substitutional impurity through the reactions

$$V_{In} + Sn_i \rightarrow Sn_{In}$$

$$V_{Ga} + Ge_i \rightarrow Ge_{Ga}$$

and the Gaussian absorption peaks observed in GaS disappear.

Conclusions

Neutron irradiated samples of InSe, GaSe, and GaS have been investigated by means of transport and optical measurements before and after isochronal annealings. The neutron transmission doping effect is observed through a drastic reduction of the resistivity in the annealed irradiated samples with respect to non-irradiated samples. The recombination of radiation induced lattice defects has been proved through the recovery of the intrinsic features in the optical absorption edge.

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