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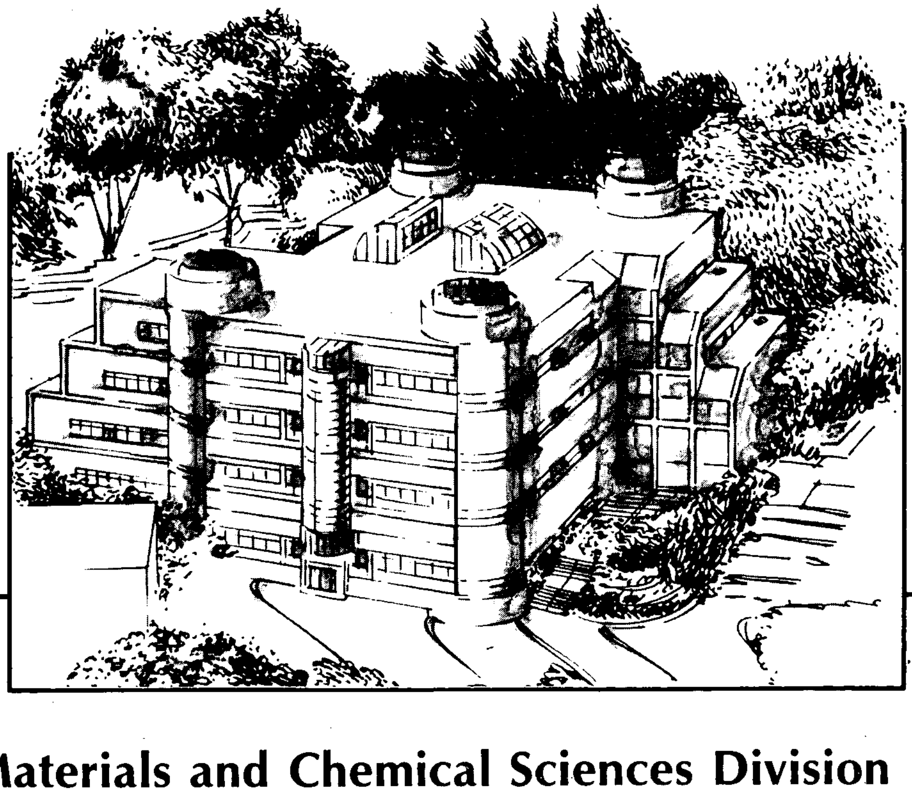

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Large Persistent Photochromic Effect Due to DX Centers in AlSb Doped with Selenium

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LARGE PERSISTENT PHOTOCHROMIC EFFECT DUE TO DX CENTERS IN ALSB DOPED WITH SELENIUM

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ABSTRACT

A large photochromic effect has been observed in bulk AlSb crystals doped with Se. Illumination with the light of energy higher than 1 eV leads to an increase of the absorption coefficient in the spectral range 0.1 eV to 1.6 eV. The enhanced absorption is persistent at the temperatures below about 100 K. The effect is a manifestation of a DX–like bistability of Se donors. The illumination transfers the electrons from the DX center to a metastable hydrogenic level. The increased absorption with peaks around 0.2 eV and 0.5 eV is due to photoionization from the donor level to X_1 and X_3 minima of the conduction band

INTRODUCTION

The DX centers are highly localized impurity related defects. They were observed in a number of III–V and II–VI semiconductors [1–4]. Their interesting and unique properties attracted a considerable attention in recent years. Besides very extensive studies of the basic properties of the defects it has been suggested and practically demonstrated [5,6] that the persistent photoconductivity effect associated with DX centers could be utilized for optical memory devices. One of the most remarkable properties of the DX centers is their bistable behavior. It has been shown [2] that intentionally introduced donors can act as substitutional effective mass shallow dopants or, under specific circumstances, they can undergo a structural relaxation forming highly localized defect centers. $Al_xGa_{1-x}As$ alloys were among the most extensively studied materials systems. Although much less effort was directed towards other semiconductors there is a clear evidence for DX defects in GaAsP, InGaP, InGaAlP and AlGaSb alloys [3].

In this paper we present the results of our studies of Se DX center in AlSb. We show that this impurity exhibits some unusual and unique properties different from the properties of donor impurities in other III–V compounds.

EXPERIMENTAL

The AlSb crystals were grown by the Czochralski technique from a selenium doped melt. The growth was carried out under Ar pressure of 4 atm. using an initially non–stoichiometric melt enriched with Sb to 0.515 atom fraction. Undoped AlSb crystals always show p–type conductivity. A series of crystals were grown with different concentration of Se added to the melt. The Se doping produces n–type material with the room temperature electron concentration as high as $3x10^{17}$ cm^{-3}.

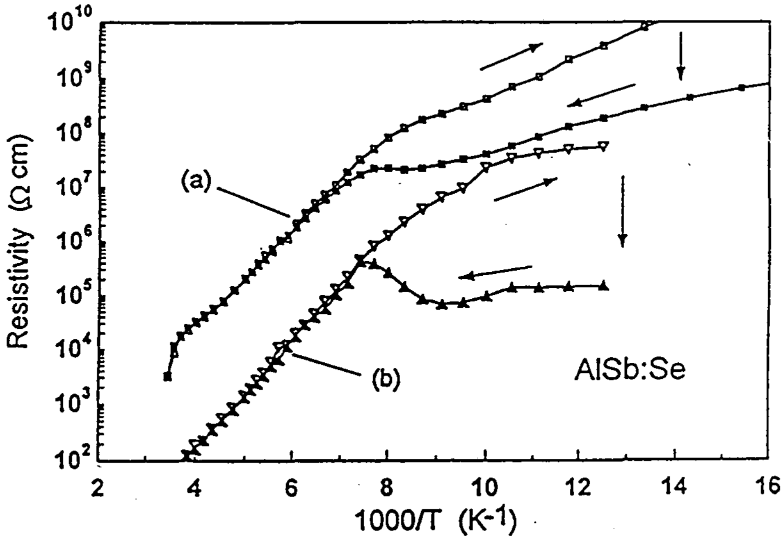

Fig. 1 Resistivity vs. temperature in two AlSb samples with different Se concentrations. The open squares represent cooling in the dark while the full squares represent the heating cycle after illumination at 77K. The difference between those two curves is a measure of the persistent photoconductivity.

Temperature dependence of the resistivity for two samples with different Se concentration is shown in Fig. 1. The resistivity is increasing rapidly with decreasing temperature. The activation energy of about 180 meV has been determined from the slope at high temperatures. A change of the slope is observed for the temperatures lower than 120 K. Illumination of the samples with white light at the low temperatures resulted in a reduction of the resistivity which persisted after the light has been switched off. The saturation value of the persistent photoconductivity (PPC) at 77 K corresponded to an increase of the electron concentration to about 10^{13} cm^{-3}. The PPC effect starts to decrease for temperature higher than 100 K and disappears at about 125K. The persistent effects are typical manifestation of the bistable behavior of DX centers and were routinely observed in other compound semiconductors [3]. The value of the PPC is relatively small, much smaller than PPC observed in the direct gap AlGaAs alloys. It is however quite typical for the indirect gap materials with a large binding energy of the effective mass donors.

Much more pronounced and interesting effects are found in the photoinduced absorption spectrum. As is seen in Fig. 2 a very small infrared absorption is observed in the sample cooled in the dark. Illumination with white light dramatically increases the absorption in the spectral range 0.1 eV to 1.6 eV. The absorption spectrum consists of two broad maxima at 0.2 eV and 0.5

eV and the absorption coefficient exceeds 50 cm^{-1} in the whole spectral range. This photochromic effect is much large than that observed in AlGaAs alloys [7]. The absorption remains low for $h\nu < 0.1$ eV. This is in agreement with electrical measurements which show a very small free carrier concentration at this low temperature. The photoinduced absorption is persistent at the temperatures below 100 K but it quickly vanishes at higher temperatures.

The excitation spectrum of the persistent optical absorption is shown in Fig. 3. The spectrum has been normalized to a constant photon flux. It was determined at 77 K from the initial slope of the photo–induced change in the absorption coefficient, $(d\Delta\alpha/dt)|_{t=0}$, measured point by point starting with the sample cooled in the dark after a complete thermal recovery of the low absorption state. The excitation spectrum, with the threshold energy of about 1 eV is very similar to the photoionization cross section for the ground DX state involving large lattice relaxation in AlGaAs [3]. The estimated value of the optical cross–section , σ_0, is about 10^{-18} cm^2 for $h\nu = 1.3$ eV This agrees very well with typical values reported for the DX centers in other materials [3].

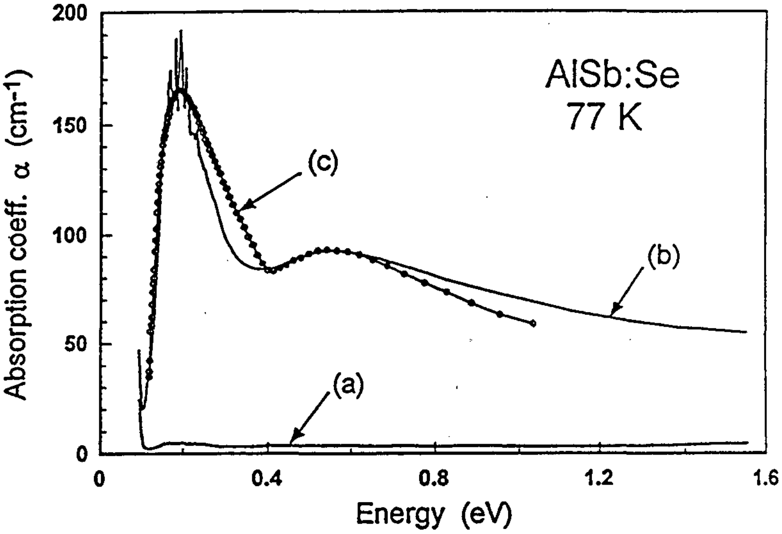

Fig. 2 Optical absorption in AlSb:Se at 77K. Absorption spectrum of the sample cooled in the dark (a) and after 15s illumination with a halogen light (b). The curve represents the calculated absorption coefficient.

The very large persistent optical absorption caused non–exponential excitation transients and long tails due to a decrease of the photon flux available for excitation. To alleviate this problem and to satisfy the requirement $\Delta\alpha\, d < 1$ the transient measurements were performed on a thin sample, $d = 0.2$ mm with lower Se concentration $n_{300} = 2x10^{16}$ cm^{-3}. The results in the insert of Fig. 3 prove a single exponential character of the excitation process. Thus, the photoinduced transfer from low to high absorption states is governed by the first order rate equation and the time constant $\tau = (\Phi\sigma_{eff})^{-1}$, where Φ is the photon flux incident on the sample and σ_{eff} is the effective optical cross section for the white light illumination.

DISCUSSION

The observed effects can be understood in terms of the DX–like bistability of Se donors in AlSb. A configuration–coordinate diagram for a donor impurity which can undergo a structural transformation into a DX–like state is shown in Fig. 4. The DX–like configuration is the ground state for the donor system. The DX level is located at the energy, E_{DX}, below the conduction band minimum. Lowering of the energy of the DX center is a result of the lattice relaxation around the Se impurity. The metastable, hydrogenic–like state of a substitutional donor is located at E_D below the lowest conduction band minimum X_1. In AlSb, the closest higher minimum of the same symmetry, X_3, is separated from X_1 by the energy, δ.

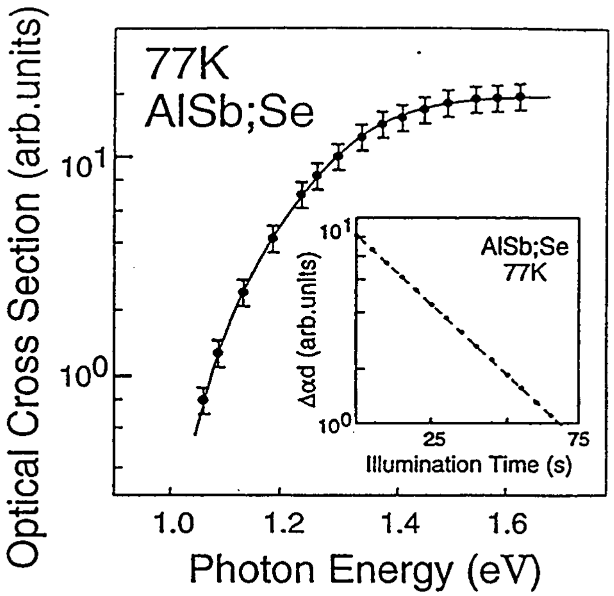

Fig. 3 The spectral dependence of the optical cross–section for the excitation of the persistent absorption. The insert shows the excitation kinetics of the absorption under white light illumniation. All measurements were done at 77K.

The two slopes of the resistivity vs. inverse temperature curve shown in Fig. 1 represent the thermal activation from the DX level and from the hydrogenic donor, D. When an AlSb:Se sample is cooled in the dark, most of the electrons freeze–out onto the DX level with only a small fraction being trapped on the metastable hydrogenic donor level. Therefore the high temperature slope of about 180 meV in Fig. 1 represents the binding energy of the DX center. Illumination with a photon energy higher than the threshold value of $h\nu_{th}$ = 1 eV transfers the electrons from the DX centers to the conduction band. At low temperatures, these electrons are then trapped at the donor level, E_D. The increased occupancy of E_D leads to a higher absorption due to the photoionization transitions from E_D to X_1 to X_3 minima in the conduction band.

Curve c in Fig. 2 represents the calculated photoionization cross–section for the transition from the donor level to X_1 and X_3 minima of the conduction band. The best fit was obtained with $E_D = E(X_1) - 110$ meV and the separation between the minima $\delta = E(X_3) - E(X_1) = 290$ meV. Our value for the binding energy of Se donors is lower than 146 meV previously determined from the absorption spectra of lightly doped AlSb [8]. The value of δ is in a good agreement with the conduction band splitting as determined from intra subband infrared absorption [9].

The large persistent photochromic effect offers a possibility of using AlSb:Se for photodiffractive applications [10]. As is seen in Fig. 2 one can produce an absorption gratings with the modulation amplitude of the absorption coefficient $\Delta\alpha > 50\ \mathrm{cm}^{-1}$. The diffraction efficiency of the absorption gratings is given by [11],

$$\eta = \exp(-\alpha d)(\Delta\alpha L_{int}/4\cos\theta)^2 \tag{1}$$

where the interaction length $L_{int} = (1-\exp(-\alpha d))/\alpha$, d is the thickness of the sample, θ is the half–angle between intersecting laser beams and α is the absorption coefficient.

For $\Delta\alpha = \alpha = 50\ \mathrm{cm}^{-1}$ and the sample thickness of 2×10^{-2} cm the photodiffractive efficiency of about 0.9 % is expected. These expectations have been recently confirmed by a Purdue group where a diffraction efficiency of about 1% has been observed using the four–wave–mixing technique [12]. The result can be compared with previous reports of photodiffractive effect in GaAs:Cr and InP:Fe where 1 to 2 orders lower diffraction efficiencies were observed [10]. Since both the sample thickness and the absorption coefficient can be independently controlled in the bulk AlSb it should be possible to optimize the parameters to achieve the theoretical efficiency limit of 6 % [12].

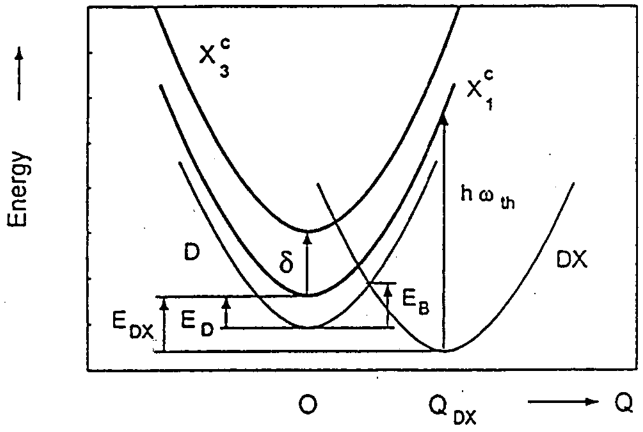

Fig. 4 Schematic representation of the configuration coordinate diagram describing the metastable behavior of the Se donors in AlSb

CONCLUSIONS

We have found that Se doped AlSb exhibits a very large photoinduced, persistent absorption. The absorption results from the photoionization of electrons from the metastable hydrogenic Se donor to the conduction band and is induced by optical transfer of electrons from the DX center to the hydrogenic Se donor. Because of the characteristic conduction band structure with two closely lying minima the absorption extends over a very broad spectral range from 0.1 eV to 1.6 eV. The persistent photo–induced absorption in AlSb:Se is the largest photochromic effect observed in any of III–V semiconductors. This effect could potentially find applications in photodiffractive devices.

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