DX CENTERS IN Al$_{0.34}$Ga$_{0.66}$As AMORPHOUS THIN FILMS

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Al$_{0.34}$Ga$_{0.66}$As amorphous thin films doped with Si have been prepared for studying common features of DX type of defects in crystalline and amorphous semiconductors. We have observed in these materials the persistent photoconductivity (PPC) effect at T < 250 K. The four energies which characterize the DX levels in these materials have been determined. A large Stokes shift with a value which is comparable with that of DX centers in crystalline Al$_x$Ga$_{1-x}$As has been observed. Our results suggest that the existence of the DX centers as well as of PPC is not simply a consequence of the band structure. Our results also suggest that there may exist a common description for DX type defects in crystalline and amorphous semiconductors.

Deep donor levels or the DX centers in semiconductors have been studied extensively in the past two decades. Substantial advances in our understanding of the DX centers have been achieved through the investigations of their properties in crystalline Al$_x$Ga$_{1-x}$As with different AlAs mole fractions.[1-2] However, there are still many fundamental questions which remain to be answered before we can have a complete physical picture for the DX centers. DX centers in Al$_x$Ga$_{1-x}$As exhibit a very interesting property at low temperatures (below 150 K) - persistent photoconductivity (PPC), the phenomenon of light induced conductivity that persists for a very long period of time after the removal of light excitation.[3,4] PPC has also been observed in many other materials, such as in II-VI semiconductors,[5,6] in SiC,[7] and in amorphous Si.[8] Different PPC behaviors in doped and undoped semiconductors have been distinguished. It is believed that all DX centers in different types of semiconductors exhibit a common feature at low temperatures, i.e. PPC. However, comparison experiments for defects as well as PPC in amorphous and in crystalline semiconductors hardly been studied. Recently, Redfield and Bube[9] proposed that light induced defects in amorphous Si and DX centers in crystalline AlGaAs may have similar origins.

In this paper, we will address two basic questions. First, how will the lattice relaxation properties of the DX centers be affected if we change the crystal structure? This is achieved by doping Si in amorphous Al$_x$Ga$_{1-x}$As. In amorphous structures, due to the disorder, one expects that the microscopic configuration around the DX centers, e.g. the number of bonds, the bond length, and the interaction between electron and impurity, is different from that of DX centers in crystalline structures. The change of microscopic configuration around the DX centers can also affect local vibrational modes. These in turn may affect the lattice relaxation properties of DX centers. The second purpose is to investigate experimentally the connection between the DX type of defect in crystalline and in amorphous semiconductors.

The samples used for this work were grown by metal-organic chemical vapor deposition (MOCVD) by Spire Corporation. Al$_{0.34}$Ga$_{0.66}$As thin films of thickness of about 2 μm were deposited directly onto quartz substrates. The growth conditions for these samples were the same as for the epitaxy grown crystalline Al$_x$Ga$_{1-x}$As.

The Si doping concentration was 3 x 10^{17} cm^{-3} and the structure of the prepared samples was confirmed to be amorphous by X - ray measurements.

Two indium spots of 1 mm in diameter and about 3 mm apart were deposited on the sample surface, gold leads were then soldered onto these two indium spots. The samples were then attached to a copper sample holder, which was placed inside a closed-cycle He refrigerator. A 36 volts bias was applied for the conductivity measurements and the dark current at room temperature was about 50 μA. A temperature controller enabled us to stabilize the temperatures to about 0.1 K. A halogen lamp together with a monochromator and an infrared filter was used as an excitation light source. The data were taken in such a way that the system was always heated up to 500 K under vacuum to convert the illuminated sample to its initial state and then cooled down again in darkness to the temperatures of measurements. The equilibration time at each temperature was about 40 min. The excitation intensity and buildup time are fixed at different temperatures. Comparison experiments have also been carried out for the Si doped crystalline Al$_x$Ga$_{1-x}$As and a 0.2 volts bias was applied to the two contacts of about 3 mm apart and the dark current at room temperature was about 2 mA.

We have observed that the DX centers in amorphous AlGaAs materials exhibit a PPC effect up to about 250 K. The properties of DX centers in these materials have been investigated through the use of PPC at different temperatures. Fig. 1 shows normalized PPC decay curves obtained at three representative temperatures. In these plots, the dark current has been subtracted from the data points and the PPC has been normalized to unity at t=0, the moment at which light excitation has been terminated. One can see that the decay rate of PPC increases with an increase of temperature and that the PPC relaxation can be characterized by a stretched-exponential function,

$$I_{PPC}(t) = I_{PPC}(0)\exp[-(t/\tau)^\beta], \quad 0 < \beta < 1 \quad (1)$$

where $I_{PPC}(t)$ is the photocurrent at time t, $I_{PPC}(0)$ the photocurrent at t=0, τ the decay time constant and β the decay exponent. The stretched-exponential PPC relaxation behavior has also been observed in crystalline Al$_x$Ga$_{1-x}$As.[10] However, the low temperature decay time constants
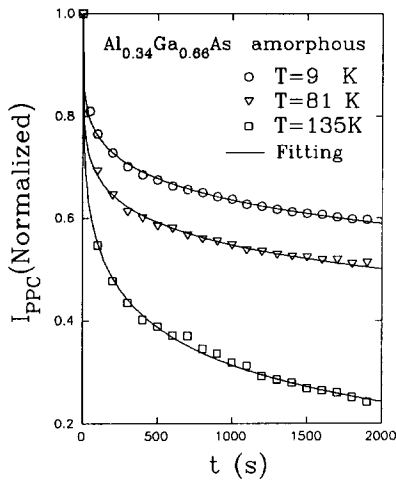
Fig. 1 PPC decay curves at three representative temperatures. The solid lines are the least square fitting by the stretched-exponential functions of Eq. (1). Data points have been subtracted from the dark level and curves have been normalized to unity at t=0, the moment the light excitation is terminated. Here, the dark and buildup currents, respectively, are 5.3 μA and 7.1 μA for 9 K, 10.4 μA and 13.9 μA for 81 K, and 17.5 μA and 19.6 μA for 135 K.
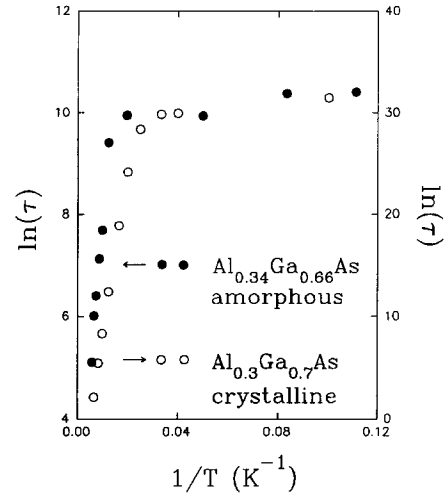

Fig. 2 Plots of ln τ vs 1/T for amorphous (● ● ●) and crystalline (o o o) $Al_xGa_{1-x}As$.

in amorphous materials are smaller than the decay time constants observed in crystalline $Al_xGa_{1-x}As$. The decay time constant τ at different temperatures has been determined by fitting PPC decay data with Eq. (1). Fig. 2 presents a plot of lnτ versus 1/T for the amorphous and a crystalline AlGaAs materials. Notice different scales of τ for the amorphous and the crystalline structures. The sharp feature observed here is that the temperature dependence of τ is similar for both the crystalline and amorphous materials. This implies that the electron capture mechanisms involved must be the same for DX centers regardless of the crystal structure. One can see that at temperatures T > 50 K, the decay time constant τ has an activated temperature dependence of the form $\tau=\tau_\infty \exp(E_C/kT)$, where τ_∞ is a prefactor representing the PPC decay time constant at T → ∞ and E_C the electron capture barrier. At low temperatures, a weakly temperature dependent capture rate has been observed in both types of materials, which agrees with a previous theoretical prediction.[11] We have to point out that prior to our measurements all previous measured values of capture time constant τ, based on which the capture barriers were deduced, have been determined from the 1/2 - or 1/e - signal point. However, at T < 80 K, the PPC decay time constants in crystalline $Al_xGa_{1-x}As$ become extremely long. In Ref. (10), we showed that the PPC in crystalline $Al_{0.3}Ga_{0.7}As$ is still more than 98% of its initial value after a 3000 seconds of decay time at low temperatures. So it is not possible to wait until the signal decays to 1/2. Therefore, fitting with stretched-exponential functions provides us with a possible access for obtaining the decay parameters in entire temperature region. Although the physical origin of stretched-exponential decay is not yet understood, the temperature dependence of τ shown in Fig. 2 is fully consistent with the theoretical prediction for DX type defects.[11] This indicates that the decay time constant τ obtained by fitting with stretched-exponential functions is directly associated with the electron capture

rate. We believe that by utilizing the same approach, the comparison between the amorphous and crystalline AlGaAs should be valid.

The significant results obtained in Fig. 2 are threefold. First, the electron capture barrier calculated from the thermally activated temperature region is about 44 meV for the amorphous materials, which is about a factor of 4 smaller than that of the crystalline AlGaAs obtained from the same measurement technique as shown in Fig. 2. It is understood that the existence of PPC is a consequence of the large electron capture barrier. It has been concluded from the hydrostatic pressure experiments that the variation of the capture barrier with alloy composition is due to the changing of band structure.[2] It is very surprising that the 44 meV capture barrier observed here could leads to PPC with such long lifetimes (∼ 10^6 s at T=9 K). Secondly, compared with the case of crystalline structure, the electron capture cross-section
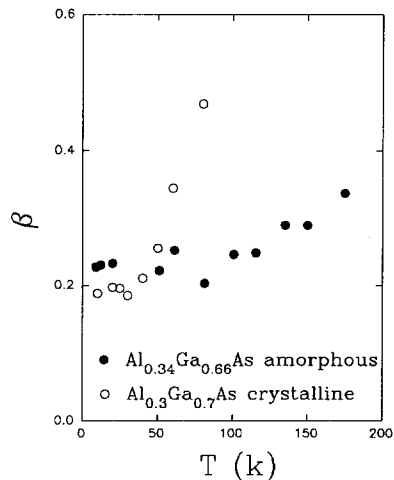

Fig. 3 Decay exponent β versus temperature.

at T → 0, σ_{n0}, is enhanced by about 8 orders of magnitude in the amorphous structure. This implies that the electronic wavefunction overlap for the states of the electrons in the conduction band and DX centers is much larger in the amorphous structure. Thirdly, the extrapolation of experimental data in Fig. 2 to infinite temperature gives a larger value of the prefactor τ_∞ for the amorphous materials.

The dependence of the decay exponent β on temperature has also been obtained as shown in Fig. 3. One sees that β increases almost linearly with temperature in the thermally activated capture region and is nearly independent of temperature in the low temperature region. This behavior is again similar to that obtained for crystalline samples. However, the increase of β versus T is less steep in amorphous materials.

The relative dark carrier concentration has been measured at different temperatures, from which a binding energy of DX centers in these materials has been obtained (about 100 meV). This binding energy is comparable with that of the crystalline samples of the same composition. This binding energy, together with the measured thermal capture barrier of 44 meV, gives a thermal emission energy, E_e, of DX centers in amorphous AlGaAs to be about 144 meV.

Another very important parameter that characterizes the DX level in these materials is the Stokes shift, which is thought to be the lattice relaxation energy when a DX center captures an electron. The optical ionization energy has been extensively studied for DX centers in crystalline Al$_x$Ga$_{1-x}$As in which a Stokes shift of about 1 eV has been confirmed. We have determined the relative photoionization cross-section of DX centers in amorphous Al$_{0.34}$Ga$_{0.66}$As from the persistent photoconductivity buildup transients at 9 K. After taking into account all experimental factors, such as the monochromator grating efficiency and the blackbody radiation efficiency of the halogen lamp, we present the final results in Fig. 4. A photoionization energy, E_0, of about 1.0 eV has been observed. These results provide a Stokes shift of about 0.9 eV, which is about the same as the value obtained for the crystalline Al$_x$Ga$_{1-x}$As.

By comparing the DX center properties in amorphous and crystalline structures, we see that their features are very similar, e.g. the PPC effect and a large

Fig. 4 Relative photoionization cross section of DX centers in amorphous Al$_{0.34}$Ga$_{0.66}$As.

Stokes shift. Furthermore, by comparing the four energies - thermal capture and emission barriers, the donor binding energy, and the optical ionization energy of the DX centers in both types of crystal structures, one sees that a change in crystal structure results in only changes in thermal capture and emission barriers. Our results then indicate that, using the large lattice relaxation picture, a change of crystal structure from crystalline to amorphous only changes the curvature of the adiabatic potential associated with the DX level ($\sim 1/2kq^2$ with k being the force constant and q the displacement in the coordinate space), but not its position.

Many interesting questions arise from our investigation. Presently, the common understanding is that the large lattice relaxation associated with the DX centers is caused by the distortion of impurity position from the normal lattice site when the DX center captures an electron.[12] For crystalline Al$_x$Ga$_{1-x}$As, the energy configuration of the DX center depends strongly on the band structure, or AlAs fraction, x. As a consequence, at x > 0.23, the DX centers in Al$_x$Ga$_{1-x}$As exhibit a large Stokes shift and the PPC effect. However, our results indicate that the Si donor atoms in amorphous AlGaAs exhibit similar properties as those in crystalline AlGaAs. Since the lattice sites are not as well defined in amorphous semiconductors as those in crystalline semiconductors, then the question arises is that what is the physical meaning of lattice relaxation in amorphous AlGaAs? Secondly, since the concept of the band structure of amorphous semiconductors is not as clear as that of crystalline semiconductors, our results seem to indicate that the band structure is not the sole criterion for the PPC effect. Thirdly, our results seem to be consistent with a recent theoretical model which suggests that there may exist a common description for DX type defects in crystalline and amorphous semiconductors.[9] By considering these factors, we think that the symmetry properties around the impurity centers may be a dominant determination factor for the existence of DX centers as well as of PPC. Symmetry breaking, either by alloying, application of hydrostatic pressure, or by changing the crystal structure, may induce the DX type of defect as well as PPC. More theoretical and experimental investigations are needed in order to answer these questions. Nevertheless, similar features observed in Si-doped amorphous and crystalline AlGaAs here suggest that, at least in impurity doped semiconductors, there may exist a common description for DX type defects in both types of crystal structures.

The reduction in capture and emission barriers indicates that the curvature of the adiabatic potential associated with the DX level becomes less steep, i.e. the effective force constant is reduced in amorphous structure. This implies that the coupling between the electron and phonon becomes weaker, which can be understood because the bonding is weaker in amorphous structures. At low temperatures, the electron capture is due to tunneling from the conduction band (or from the shallow donor level) to the DX level and the capture rate has been predicted to be nearly temperature independent with the form[11,13]

$$\sigma_n = \sigma_{n0}(N+1)^p e^{-2NS}, \qquad (2)$$

where $p\hbar\omega$ is the net donor binding energy E_0, $\hbar\omega$ the phonon energy, N the phonon population, and S the electron-phonon coupling constant. Here σ_{n0} is the capture cross section at temperature T=0 (N=0, at T=0) and is related to S by

$$\sigma_{n0} \sim S^p e^{-S}. \qquad (3)$$
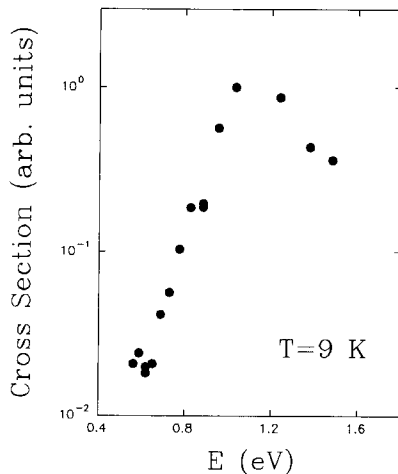
From Eq. (3), one can see that the observed 8 orders of

magnitude reduction in σ_{n0} in amorphous structure cannot be solely attributed to the changing of S. However, it can be understood if we consider the following: in amorphous structures, the force constant k of the adiabatic potential $U = 1/2 kq^2$ is reduced, which implies that the vibrational energy, $\hbar\omega$, is also decreased. Since the binding energy E_0 is comparable for the amorphous and crystalline structures, decreasing $\hbar\omega$ means an increase of p. The expression for the coupling parameter S is given by,[11,13]

$$S = (1/2)kq_0^2/\hbar\omega, \qquad (4)$$

where q_0 is the displacement of the DX center at the potential minimum with respect to the conduction band minimum in the configurational space. If we approximate the adiabatic potential with the potential of an harmonic oscillator, then $\omega \propto k^{1/2}$. If k decreases by a factor of n, $\hbar\omega$ is decreased by a factor of $n^{1/2}$ and so is S. However, p is increased by a factor of $n^{1/2}$. This could result in an increase of σ_{n0} by many orders of magnitude according to Eq. (3). The observed increase of τ_∞ for the amorphous structure, implying a decreasing of the capture cross section at $T \to \infty$, is due to the decrease of the electron-phonon coupling strengths.

In conclusion, common properties of DX centers have been investigated in amorphous and in crystalline AlGaAs through the use of PPC. In comparison with crystalline AlGaAs, our results can be summarized as follows: (a) DX centers in amorphous structure exhibit the PPC effect as well as a large Stokes shift, just as in the crystalline structure; (b) the capture and emission barriers associated with the DX centers in amorphous AlGaAs are smaller; (c) the net binding energy and the optical ionization energy, and therefore the Stokes shift, are insensitive to the crystal structure; (d) in amorphous AlGaAs, the coupling between the electron and phonon is weaker. Our experimental results seem to suggest that the dependence of the electron capture barrier on the band structure is not the sole criterion for the observation of PPC in Si-doped AlGaAs materials. Additionally, the results seem also to indicate that a common description for the DX type of defect in amorphous and crystalline semiconductors may exist.

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