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Substitutionality of Te- and Sn-related *DX* centers in $Al_xGa_{1-x}As$

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The lattice locations of Te and Sn atoms forming *DX* centers in $Al_xGa_{1-x}As$ were determined by particle-induced x-ray emission and ion-beam-channeling methods. The Te atoms were found to be in the As substitutional sites while the Sn atoms were in the Ga(Al) sites. No off-center displacement of Te and Sn larger than 0.14 Å from the substitutional sites was observed in either system.

Recently a considerable amount of experimental and theoretical attention has been directed toward the understanding of the microscopic origin of *DX* centers in *n*-type $Al_xGa_{1-x}As$ ($x > 0.23$). The *DX* centers account for low-temperature persistent photoconductivity in *n*-type $Al_xGa_{1-x}As$ and exhibit a large Franck-Condon shift[1] (i.e., the photoionization threshold is much greater than the thermal depth). Most authors agree that these defects are a deep state of usually shallow donors, such as Si, Sn, Se, and Te in $Al_xGa_{1-x}As$, but the microscopic explanation of the large carrier-capture barrier and Franck-Condon shift is still highly controversial.

The properties of the *DX* centers were originally explained by Lang[1] with a configuration coordinate model. According to this model, the *DX* center undergoes a distortion when it traps an electron. However, the nature of this distortion (i.e., whether it is an off-center T_2 displacement, a fully symmetric A_1 breathing distortion, or a bond-bending E motion) remains unclear, even though a large number of theoretical models has been proposed, most of which assumed an off-center displacement of either the dopant atoms or the nearest-neighbor atoms (Ga or Al).[1-4] Recently, Mizuta and Kitano[5] carried out a fluorescence extended x-ray-absorption fine-structure (EXAFS) experiment to investigate directly the local environment of the *DX* center in $Al_{0.38}Ga_{0.62}As$:Se. Their results showed no change in bond lengths of Se donors upon photoionization within the sensitivity limit of 0.04 Å of the EXAFS techniques.

This paper reports a new approach to the question of the lattice location of *DX* centers by a different technique, particle-induced x-ray emission (PIXE) combined with ion channeling. The off-center displacements of the dopants in $Al_{0.42}Ga_{0.58}As$:Te and $Al_{0.41}Ga_{0.59}As$:Sn were investigated. In a PIXE and channeling experiment, a $^4He^+$ ion beam is aligned with an axial channel of the crystal, e.g., the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions. χ_{min}, the ratio of the x-ray yield when the beam is exactly aligned with a channel to the yield when the beam is incident on the target in a random direction, is measured for both the dopant atoms and the host atoms. X-ray yields of the dopant and host atoms are also measured as a function of deviation of the particle incidence direction from the channeling crystallographic axis. The angle for which the characteristic x-ray yield is equal to half of the random value (alignment far from the axial channel) is called the critical half-angle $\psi_{1/2}$. Substitutionality of the dopants is investigated by comparing the $\psi_{1/2}$ and the χ_{min} of the host and the dopant signals.[6]

In this work, Te- and Sn-doped $Al_xGa_{1-x}As$ were chosen since Te and Sn represent two types of different donors in $Al_xGa_{1-x}As$, Te being a group-VI dopant substitutes the As in the host lattice, while Sn being a group-IV dopant preferentially occupies the Ga site. Besides, Te donors in all $Al_xGa_{1-x}As$ films and Sn donors in films grown by molecular-beam epitaxy (MBE) are completely nonamphoteric species,[7] so the complication of self-compensation can be avoided. The experiments were done at room temperature so that even if a particle ionizes the *DX* center, recapture of an electron would be instantaneous.

The alloy compositions and dopant concentrations were measured by PIXE and Rutherford backscattering spectrometry (RBS). PIXE and RBS measurements were carried out using 1.8- and 1.5-MeV $^4He^+$ beams for the Sn- and Te-doped samples, respectively. A silicon surface-barrier detector is positioned at 165° with respect to the ion beam for charged-particle detection. X rays emitted from the target are detected by a Si(Li) detector positioned at 30° to the beam. The alignment of the sample is monitored by observing the yield of the particles backscattered from within ~300 Å of the surface layer of the sample as the sample is tilted with respect to the ion beam. A dose of 5 μC was accumulated for each spectrum with a beam current of ~10 nA. To minimize beam damage, the sample was translated after approximately 30-μC beam exposure.

First, an $Al_xGa_{1-x}As$:Te 10-μm-thick layer was measured. The layer was grown by metal-organic chemical-vapor deposition (MOCVD) on a semi-insulating GaAs substrate. PIXE and RBS measurements revealed a total concentration of Te atoms of $\sim 3\times10^{18}/cm^3$. Simultaneously the alloy composition was determined to be $Al_{0.42}Ga_{0.58}As$. The donor concentration $N_D-N_A=3.6\times10^{18}/cm^3$ was directly measured by capacitance-voltage analysis with a Au Schottky contact and the concentration of paramagnetic donors $N_p=3.1\times10^{18}/cm^3$ by magnetic-susceptibility measurements.[8] This close agreement of the total Te atom concentration with N_D-N_A and N_p indicates a very low degree of compensation. Simulation of ion-solid interactions using the TRIM computer program[9] shows that the damage due to the ion beam concentrates mainly at the end of the range of the ions (≈ 5.5 μm). However, 99% of the x rays emitted by the Te atoms comes from the 2.5 μm immediately below the surface where the ion-beam damage is negligible (the average energy transferred to the dopant atoms by the ion beam in the region within 2.5 μm of the surface is only $\approx$ 20–30 meV/Å). The Hall-effect measurement gave a value of room-temperature electron concentration of $3.2\times10^{17}/cm^3$, indicating that only 10% of Te donors are ionized at room temperature, whereas the other 90% should be *DX* centers in the neutral charge state. Thus the PIXE measurement indeed probes the lattice location of the *DX* centers in their neutral ground state.

The angular scans of the Te *L*, Ga *Kα*, and As *Kα* x-rays through the ⟨100⟩ axis and the ⟨110⟩ axis in a {110} plane of the sample are shown in Figs. 1(a) and 1(b). The values of the χ_{min} and $\psi_{1/2}$ are tabulated in Table I. Calculations show that although absorption of the Te and Sn *L* x rays in the $Al_xGa_{1-x}As$ is considerably larger than that of the Ga and As *K* x rays, the ionization cross sections of the *L*'s decrease much more slowly as a function of depth in the sample comparing to those of the *K*'s. The net effect is that the mean emission depth of the various x rays are the same to within 5%. Note that in Table I, the $\psi_{1/2}$(Ga) differs considerably from the $\psi_{1/2}$(As) across the ⟨110⟩ axis. This arises from the fact that along the ⟨110⟩ direction, the Ga(Al) and As atoms form separate rows.[10] Since $\psi_{1/2}\sim Z_2^{1/2}$, where Z_2 is the atomic numbers of the crystal atoms, the values of the $\psi_{1/2}$ for scans arising from the Ga(Al) and As strings should be different.

From Fig. 1 and Table I we notice that χ_{min} for Te *L* x rays in both ⟨100⟩ and ⟨110⟩ alignment are slightly higher than those of the host As *Kα* x rays. Considering the statistical error (~5%), one can conclude that the Te atoms in the layer are mostly substitutional. In fact, following the analysis given in Williams, Barnes, and Feldman,[11] we find that 92% of the Te atoms are substitutional in the $Al_{0.42}Ga_{0.58}As$ epilayer. From Fig. 1 we also observe that the Te x-ray angular scans follow the host-lattice As x-ray scans very well. The $\psi_{1/2}$(Te) across the ⟨100⟩ and ⟨110⟩ axes are identical to the $\psi_{1/2}$(As) to within 0.02° accuracy. Using the continuum model formulated by Lindhard,[12] the displacement of the dopant atoms from a substitutional site r_x can be related to the ratio of the critical half-angle for the dopant $\psi_{1/2}^D$ to that of the host $\psi_{1/2}^H$ by the following expression:[6]

$$(\psi_{1/2}^D/\psi_{1/2}^H)^2=\ln[(Ca/r_x)^2+1]/\ln[(Ca/\rho)^2+1]\,, \qquad (1)$$

where C^2 is usually taken equal to 3, a is the Thomas-

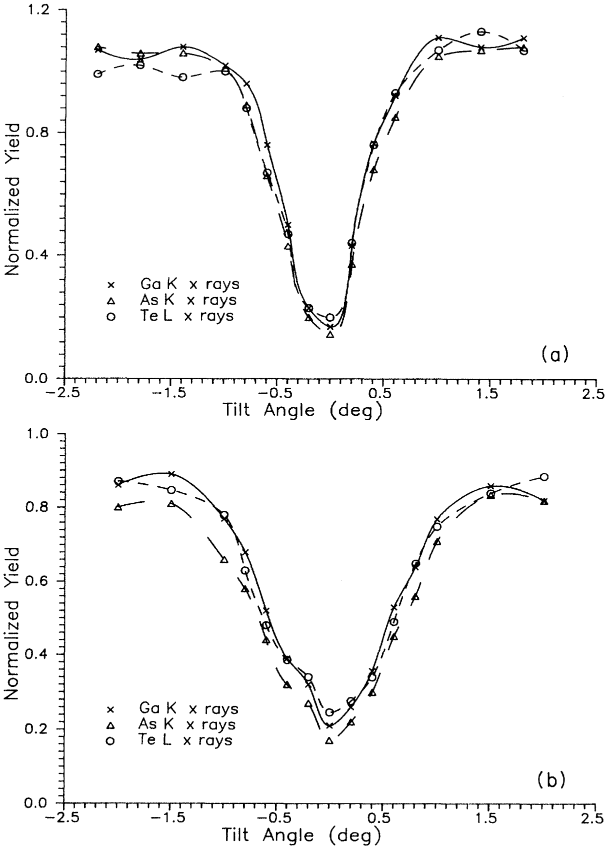

FIG. 1. The angular scans of the Te *L* (o), Ga *Kα* (×), and As *Kα* (Δ) x rays excited by 1.5-MeV $^4He^+$ through the (a) ⟨100⟩ axis, and (b) ⟨110⟩ axis along a {110} plane.

TABLE I. Summary of the measured values of the critical half angle $\psi_{1/2}$ and the minimum yield χ_{min} for the RBS signals and the Ga *Kα*, As *Kα*, and Te *L* x-ray signals when the beam is aligned with the ⟨100⟩ and ⟨110⟩ axes of the $Al_xGa_{1-x}As$:Te sample.

	$\psi_{1/2}$(°) (±0.02°)		χ_{min}	
	⟨100⟩	⟨110⟩	⟨100⟩	⟨110⟩
RBS	0.50	0.90	0.08	0.07
Ga *Kα*	0.37	0.61	0.17	0.21
As *Kα*	0.40	0.70	0.15	0.17
Te *L*	0.39	0.69	0.20	0.25

Fermi screening distance, and ρ is the transverse rms thermal vibration amplitude ($\rho = 0.1202$ Å). Considering the error in the $\psi_{1/2}$ measurement $\approx \pm 0.02°$, the minimum detectable displacement of the impurity in our experiment is $r_x/\rho \approx 1.2$ (or $r_x \approx 0.14$ Å). From Eq. (1) one notices that a 0.2-Å displacement into the channel corresponds to a 26% reduction in $\psi_{1/2}$ and, therefore, the channeling method is very sensitive to impurity displacement larger than ρ. The values of the $\psi_{1/2}$ for the different angular scans in Table I reveal that if there is an off-center displacement of the Te atoms in the $Al_xGa_{1-x}As$ lattice, it must be smaller than 0.14 Å. The calculated $\psi_{1/2}(Ga)/\psi_{1/2}(As)$ along the ⟨110⟩ direction is approximately 0.84, which agrees well with our experimental value (≈ 0.88). We also notice that along ⟨110⟩, $\psi_{1/2}(Te) \approx \psi_{1/2}(As)$ but differs considerably from $\psi_{1/2}(Ga)$ indicating that the Te atoms occupy the substitutional As sites.

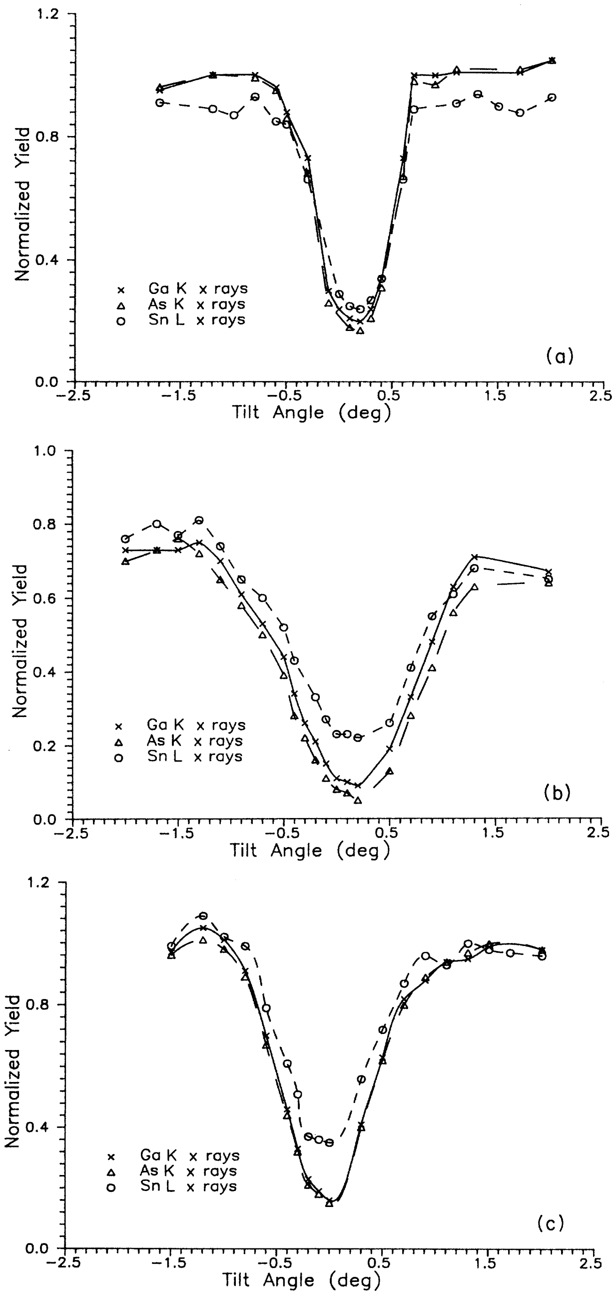

FIG. 2. The angular scans of the Sn *L* (○), Ga *Kα* (×), and As *Kα* (△) x rays excited by a 1.8-MeV $^4He^+$ ion beam through the (a) ⟨100⟩ axis, (b) ⟨110⟩ axis along a {110} plane, and (c) ⟨111⟩ axis.

RBS analysis of the MBE-grown 3.5-μm thick $Al_{0.41}Ga_{0.59}As$:Sn epilayer grown on an n^+ GaAs substrate shows accumulation of $\approx 1.5 \times 10^{14}$ Sn atoms/cm^2 on the surface of the layer. This surface Sn accumulation has been observed by many investigators in GaAs:Sn thin films. From the RBS analysis, we determine that these surface Sn atoms do not occupy any specific lattice site but are randomly distributed within 20 Å of the surface. After subtracting the x-ray yield due to these surface Sn atoms from the PIXE spectrum we find that the Sn concentration in the $Al_{0.41}Ga_{0.59}As$ layer is $\sim 6 \times 10^{18}$ atoms/cm^3.

The angular scans for a 1.8-MeV $^4He^+$ ion beam across the ⟨100⟩, ⟨110⟩, and ⟨111⟩ axial channels of the $Al_{0.41}Ga_{0.59}As$:Sn sample are shown in Fig. 2. The measured minimum yield χ_{min} and the critical half-angle $\psi_{1/2}$ for these scans are given in Table II. Following the analysis given in our previous work on GaAs:Sn,[13] the higher χ_{min} for the Sn signals in all channeling directions are consistent with the presence of the Sn atoms distributed randomly on the surface of the sample.

Aside from the higher χ_{min}, $\psi_{1/2}(Sn) = \psi_{1/2}(Ga)$ to within 0.02° accuracy. The maximum displacement of the Sn atoms from the substitutional sites as estimated by Eq. (1) with the $\psi_{1/2}$'s from Table II is about 0.13 Å which is within the uncertainty of the method. Along the ⟨110⟩ axis, $\psi_{1/2}(Sn) \approx \psi_{1/2}(Ga)$ suggesting substitutionality of the Sn atoms in the Ga(Al) sites in the lattice. Furthermore, these results on $Al_{0.41}Ga_{0.59}As$:Sn are identical to those obtained on GaAs:Sn thin films grown by MBE under similar conditions.[13] Therefore, we conclude that the substitutionality of Sn dopants in GaAs and $Al_xGa_{1-x}As$ are identical to within the resolution of the ion-channeling techniques.

In conclusion, the results of our channeling PIXE experiments clearly rule out any off-center lattice relaxation of the dopant atoms in $Al_xGa_{1-x}As$:Te and $Al_xGa_{1-x}As$:Sn larger than 0.14 Å. These results are in agreement

TABLE II. Summary of the measured values of the critical half angle $\psi_{1/2}$ and the minimum yield χ_{min} for the RBS signals and the Ga *Kα*, As *Kα*, and Sn *L* x-ray signals when the beam is aligned with the ⟨100⟩, ⟨110⟩, and ⟨111⟩ axes of the AlGaAs:Sn sample.

	$\psi_{1/2}$ (deg) (±0.02°)			χ_{min}		
	⟨100⟩	⟨110⟩	⟨111⟩	⟨100⟩	⟨110⟩	⟨111⟩
RBS	0.55	0.82	0.62	0.065	0.055	0.069
Ga *Kα*	0.39	0.61	0.48	0.20	0.09	0.16
As *Kα*	0.40	0.66	0.48	0.17	0.08	0.15
Sn *L*	0.40	0.60	0.46	0.24	0.22	0.35

with the EXAFS work by Mizuta and Kitano[5] but at variance with most theoretical models assuming a large off-center lattice relaxation involving movement of the dopant atoms.[3,4] Since the combination of PIXE and channeling cannot detect any displacement of the host atoms, our results with the $Al_xGa_{1-x}As$:Te system do not contradict the pseudopotential calculations by Chadi and Chang[2,14] on a group-VI dopant, S in $Al_xGa_{1-x}As$ where they found that one of the nearest-neighbor Ga (or Al) atoms of the S dopant moves by 1.13 Å into the interstitial position. The S atoms remain substitutional in the As sites. The results of Chadi and Chang[2,14] on a group-IV dopant, Si in $Al_xGa_{1-x}As$, however, show that the Si atom moves by 1.17 Å away from one of its nearest-neighbor As atoms, along the bond axis, into a threefold-coordinated interstitial position. Our results on $Al_xGa_{1-x}As$:Sn do not indicate such large displacement of the dopant. Although both Si and Sn are group-IV donors in $Al_xGa_{1-x}As$, they may behave differently in the lattice due to the large difference in their atomic mass and size.

The PIXE results in this paper are obviously consistent with the small lattice-relaxation models, as, e.g., proposed by Hjalmarson and Drummond.[15] However, a small lattice relaxation model was ruled out by the pressure derivatives of the emission and capture barriers of *DX* centers.[16] Therefore, it appears worthwhile considering a *large* lattice relaxation, which does *not* involve a large off-center displacement of the dopant atom. Such a model is consistent with all experimental results. The only way to reconcile the results of this work and of Mizuta and Kitano[5] (which also rule out a breathing-mode symmetric A_1 distortion) in terms of large lattice relaxation is to assume that the lattice relaxation is a bond-bending E distortion, not detectable by either EXAFS or PIXE. This is in agreement with the model proposed by Oshiyama and Ohnishi.[17]

Note added in proof. A recent experiment by Marwick, Theis, and Parker[18] showed that the resistivity of a 3-μm-thick $Al_{0.23}Ga_{0.77}As$:Sn layer increased as the layer was irradiated with a MeV $^4He^+$ beam to a total dose of 5×10^{14} ions/cm^2 corresponding to ~1.5 μC in our experiment. This result indicated that there existed beam-induced defects compensating the donors in the layer. In order to eliminate the effect of such defects on our channeling results, we have performed channeling experiments on our samples with a $^4He^+$ beam does of ~0.5 μC per spectrum (such a low beam dose on the layer does not increase the layer resistivity by more than a factor of 2 as indicated by the results of Marwick, Theis, and Parker). These low-dose channeling experiments gave results identical to those presented in this paper.

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