PHYSICAL REVIEW B

VOLUME 41, NUMBER 17

Piezospectroscopic study of interstitial oxygen in gallium arsenide

Chun-ying Song^{*} and Bernard Pajot

Groupe de Physique des Solides, Tour 23, Université Paris 7, 2 place Jussieu, 75251 Paris CEDEX 05, France

Claude Porte

Laboratoire d'Optique de la Matière Condensée, Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris CEDEX 05, France

(Received 22 March 1990)

We have measured the stress-induced splitting of two local vibrational modes of O-related centers in GaAs at 8 K for a stress parallel to a $\langle 110 \rangle$ direction and the components of their piezospectroscopic tensors. It is shown that one mode near 845 cm⁻¹ corresponding to a $\langle 111 \rangle$ -oriented dipole with a weak response to stress is associated with interstitial oxygen bonded to one Ga and one As nearest-neighbor atom. The mode near 730 cm⁻¹ corresponds to a $\langle 110 \rangle$ -oriented dipole with a larger response to stress and the related center is still an O atom bonded to two next-nearest-neighbor Ga atoms. The parallel with the oxygen-vacancy center implies also the presence of an As vacancy in this center. We report qualitative results on the reorientation under stress of these two O-related centers in GaAs in relation with possible physical origins of this effect.

Direct spectroscopic evidence of the presence of oxygen in semi-insulating (SI) GaAs crystals has been given by the observation in the infrared (ir) of local vibrational modes (LVM's) whose positions depend on the oxygen isotope considered:^{1,2} One feature near 845 cm^{-1} at liquid-helium temperature (LHeT) has been ascribed to the antisymmetric mode of the Ga-O-As entity and the most likely structure for this center seems to be an interstitial O atom (O_i) bonded to two nearest-neighbor atoms of the crystal,² but we cannot totally exclude the existence of a Ga-O-As_{Ga}, V_{As} center (V_{As} stands for the As vacancy) as the electrical behavior of non-chromium-doped SI GaAs is dominated by the presence of the EL2 defect involving an As antisite (As_{Ga}). Three other features be-tween 713 and 730 cm⁻¹ were attributed^{3,4} to different charge states of a Ga-O-Ga, V_{As} center comparable to the oxygen-vacancy center (O-V) in silicon.^{5,6} In silicon, the O-V center is produced only by irradiation with energetic particles, but Ga-O-Ga, V_{As} seems to be present in most O-containing GaAs crystals without need for irradiation. A uniaxial stress along some crystallographic direction usually lifts the orientational degeneracy of noncubic defects and splits associated vibrational lines in as many components as there are different orientations of the defect with respect to stress.⁷ This technique has allowed us to show that the dipole moment associated with the antisymmetric mode of the Si-O-Si group in silicon can be considered as parallel to the (111) direction of the Si-Si bond broken to accommodate the O atom.⁸ For an O-Vcenter, where the O atom is bonded to two next-nearestneighbor (NNN) Si atoms, the dipole moment of the antisymmetric mode is parallel to a (110) direction.⁶ We have tested these models for O-related LVM's in GaAs, whose crystal structure (zinc blende) is fundamentally the same as that of diamond by applying a uniaxial stress to oriented samples and measuring the splitting and polarization characteristics of the ir lines at LHeT. We show

here that, owing to the smaller line width of the O-related lines in GaAs as compared with silicon, it is possible to determine rather accurately the components of the piezospectroscopic tensors and the orientation of the dipole moment for the two centers. The results presented here are for a stress σ parallel to the $\langle 110 \rangle$ direction of the crystal: This orientation must simplify the observation for a trigonal center and is expected to produce the largest splitting for the O-V center; moreover, this orientation allows the determination of all the components of the piezospectroscopic tensor for $\langle 110 \rangle$ - or $\langle 111 \rangle$ -oriented defects.

The stress is applied to the sample through a home-built stress accessory fitted to an Oxford Instruments CF 204 exchange-gas cryostat. The stress splitting of the electronic 2p' line of boron in silicon at 669 cm⁻¹ measured with this system was compared to the one reported in Ref. 9 and both results agree within the accuracy of the measurements. The lowest temperature of the stressed samples was determined to be about 8 K. The spectra are obtained with a BOMEM DA3 Fourier-transform spectrometer equipped with an extended-range mercury cadmium telluride detector with an apodized resolution of 0.1 cm⁻¹.

The zero-stress spectrum of Ga-O-As in GaAs is a doublet (845.45 and 845.82 cm⁻¹ at LHeT) because either ⁶⁹Ga or ⁷¹Ga isotopes can bind to an O atom while there is only one 100% As isotope and the full width at half peak (FWHP) of the individual lines³ is ≈ 0.13 cm⁻¹. The Ga-O-Ga, V_{As} center is an O atom bonded to two NNN Ga atoms which are nearest neighbors of an As vacancy. Three vibrational features near 714, 715, and 730 cm⁻¹ labeled C (B' in Ref. 4), B, and A, respectively are related to this defect and they are presumably due to different charge states of the defect.^{3,4} Each feature consists of three sharp lines with FWHP's ≈ 0.07 cm⁻¹ and their normal relative intensities match the combined product (1, 3, and 2.3) of the abundances of the two Ga iso-

<u>41</u> 12 3 30

12331

topes. The feature investigated here is A because its concentration was the largest in our samples. The lines are labeled A_{HH} , A_{HL} , and A_{LL} where L (light) and H (heavy) correspond to the ⁶⁹Ga and ⁷¹Ga isotopes, respectively, and their positions at LHeT are 730.19, 730.68, and 731.17 cm⁻¹.

O-containing GaAs samples were cut to allow compression along the [110] direction with the viewing axis along [001]. For this geometry, the radiation can be polarized parallel to [110] or to $[1\overline{1}0]$. With polarized radiation, only one component shifted towards high or low energies for $\mathbf{E} \| \boldsymbol{\sigma}$ or $\mathbf{E} \perp \boldsymbol{\sigma}$ is observed, as shown in Fig. 1, and this indicates that for $\sigma \parallel [110]$ each line splits into two components with comparable intensities. Such a polarization behavior is expected from a trigonal center with its dipole moment along the (111) trigonal axis since, for this geometry, there are two nonequivalent classes of such centers with respect to a stress parallel to a (110) direction and the two classes lie in two mutually orthogonal {110} planes. Hence, if E lies in one of these planes it can only couple to the dipoles vibrating in the same plane. The above splitting rules out the possibility that the doublet originates from a Ga-O-As_{Ga}, V_{As} center as for this defect, the dipole moment associated with the Ga-O-AsGa entity would be along a (110) direction, with three nonequivalent classes for a stress along a (110) direction. This would result in a splitting of each line of the doublet into three partially polarized components and this is not borne out by experiment. The splitting and shift under a (110) stress of a line related to a (111) dipole can be expressed as a function of the two independent components of the piezospectroscopic tensor of the center, A_1 , representing the isotropic part of the stress and A_2 , the anisotropic part.⁷ For $\sigma \parallel [110]$, the shifts of the two components of each Ga-O-As line are then $(A_1 \pm A_2)\sigma$ and their splitting $2A_2\sigma$. Due to the complete polarization of the two components of each line, splittings comparable to



FIG. 1. Splitting and polarization characteristics of the antisymmetric mode of interstitial oxygen in GaAs at LHeT for a stress parallel to the [110] axis. The zero-stress doublet position (⁷¹Ga-¹⁶O-As and ⁶⁹Ga-¹⁶O-As) and the relative intensities of the two lines are indicated by the two bars. The propagation vector **k** of the radiation is parallel to the [001] axis. The instrumental resolution is 0.1 cm⁻¹.



FIG. 2. Splitting and polarization characteristics of the intersitial oxygen doublet in GaAs at LHeT as a function of a stress parallel to the [110] axis. The high-energy components correspond to centers with dipole moments perpendicular to the stress.

the FWHP could be measured as a function of stress at LHeT for $\sigma \| [110]$ (Fig. 2) and the piezospectroscopic coefficients A_1 and A_2 could be determined. The accuracy depends on the exact determination of the zero-stress position and on the reduction of frictions in the stress apparatus. These coefficients are given in Table I. They are larger than the ones for the same mode in silicon and seem to be slightly larger for the heavier Ga isotope. Difference between the observation conditions of the effect of stress on the O_i spectra in GaAs and silicon can be appreciated by indicating the ratios of the splitting of the two components and of their FWHP's: For $\sigma \| [110]$, this ratio is ≈ 1 for GaAs at 120 MPa against ≈ 0.2 for silicon at 350 MPa.¹⁰ The atomic configuration in GaAs is not exactly the same as in silicon where the Si₂O complex

TABLE I. Components of the piezospectroscopic tensor for the antisymmetric modes of the $\langle 111 \rangle$ -oriented ${}^{16}O_i$ centers in GaAs and silicon and of the $\langle 110 \rangle$ -oriented ${}^{16}O$ - V_{As} center A in GaAs and neutral ${}^{16}O$ -V in silicon at LHeT. The unit is cm⁻¹ GPa⁻¹.

	⁶⁹ Ga-O-As	⁷¹ Ga-O-As	Si-O-Si ^a
$\overline{A_1}$	0.17 ± 0.04	0.21 ± 0.04	0.2 ± 0.1
A_2	-0.69 ± 0.09	-0.79 ± 0.07	-0.2 ± 0.1
	Ga-O-Ga, V _{As}		Si-O-Si _{nnn} ª
A_1	2.5 ± 0.4		1.7 ± 0.3
A_2	2.5 ± 0.4		2.5 ± 0.3
A 3	5.8 ± 0.7		3.5 ± 0.3
	an 1999 in the state of the state		

^aReference 8.

12332

displays $C_{2\nu}$ symmetry, but the data obtained nonetheless indicate that the dipole moment of the antisymmetric mode of As-O-Ga can be considered as parallel to the (111) axis and that this center is identical to O_i in silicon. The small value of A_1 for $O_i (\approx 0.2 \text{ cm}^{-1}/\text{GPa})$ in both materials reflects the small compressibility of the center, related to the outward local distortion produced by the O atom on the lattice bonding. A noticeable fact is that for O_i , the coefficient A_2 is negative in both GaAs and silicon. This means that the smaller the angle between the dipole and the stress direction, the smaller the frequency of the mode. On the other hand, it is known from stress-induced dichroism of the O_i band in silicon that the configurations of least energy near or above room temperature $(\approx 450 \,^{\circ}\text{C})$ are the ones making the largest angle with the stress direction.¹¹ It can be tentatively suggested that this low-temperature effect under stress is due to some anharmonic effects for the O_i mode which could also be accounted for by the lattice distortion.

The situation is different for Ga-O-Ga, V_{As} where, for a stress along a [110] axis, each line of triplet A is split into three components (1, 2, and 3 in order of increasing energy) for unpolarized observation along a [001] viewing axis (Fig. 3). For this geometry, the central components 2 are



FIG. 3. Splitting of triplet A attributed to a Ga-O-Ga, V_{As} center in GaAs at LHeT as a function of a $\sigma \parallel [110]$ stress for a k $\parallel [001]$ viewing axis. For this geometry, components 1 and 3 are polarized E_{\perp} and $E \parallel \sigma$, respectively, and component 2 is not polarized. L stands for the light isotope ⁶⁹Ga and H for the heavy isotope ⁷¹Ga.

observed whatever the polarization, but components 1 and 3 are polarized perpendicular and parallel to σ , respectively. For stresses where the overlap can be minimized, the relative intensities of the components without polarization are roughly in a 1:2:1 ratio. For the measurements with polarized radiation, where the uncertainty is larger because of the resolution requirement, the agreement, which is only qualitative, indicates comparable intensities for components 1 and 2 or 2 and 3. These results can be interpreted by assuming that the vibrating unit responsible for feature A is a Ga-O-Ga entity whose main axis and dipole moment lie along a (110) direction. The same group-theoretic analysis as for the O_i center can be used to show that, in this situation, with unpolarized radiation, each line of the isotopic triplet must in turn split into a symmetric triplet with relative intensities 1, 2, and 1. For $\mathbf{E} \| \boldsymbol{\sigma}$, it reduces to a doublet of equal intensity, while for the $\mathbf{E} \perp \boldsymbol{\sigma}$ geometry which corresponds here to $\mathbf{E} \parallel [110]$, an equal intensity doublet is expected again. The piezospectroscopic tensor for (110) oriented centers is defined ' by three independent components A_1 , A_2 , and A_3 . For $\sigma \parallel [110]$, these components are related to the slopes C_1 , C_2 , and C_3 of the straight lines 1, 2, and 3 of Fig. 3 by $C_1 = A_2 - A_3$, $C_2 = (A_1 + A_2)/2$, and $C_3 = A_2 + A_3$, hence $A_2 = (C_1 + C_3)/2$, $A_3 = (C_3 - C_1)/2$, and $A_1 = 2C_2 - A_2$. The coefficients A_i are given in Table I for the O-V center A in GaAs and for the neutral O-V center in silicon which is also another (110) oriented center. The values of the hydrostatic component for the O-V centers (2.5 and 2.2) cm^{-1}/GPa in GaAs and in silicon, respectively) are about 1 order of magnitude larger than the ones for O_i and this could be explained by the presence of a lattice vacancy which allows a larger compressibility of the defect. Components 3, fully polarized with $\mathbf{E} \| \boldsymbol{\sigma}$ correspond to $\mathbf{O} \cdot V_{As}$ centers whose main axes are parallel to the stress and the increase of the frequency of the mode is related to the reduction of the bond length.

These results prove that, within experimental accuracy, the O-related centers giving rise to the ir features near 845 and 730 cm⁻¹ in O-containing GaAs have dipole moments parallel to $\langle 111 \rangle$ and $\langle 110 \rangle$ axes, respectively, and that they can be safely identified with interstitial oxygen and with the O- V_{As} center. Measurements of the reorientation of center A in GaAs:O were performed after applying a stress parallel to [110] at 300 K, cooling under stress at 8 K and removing the stress. Preliminary results show a stress-induced dichroism dependent on the Fermi level in the sample: One sample where only state A was present showed practically no dichroism while another sample where the A, B, and C states coexisted exhibited a pronounced dichroism of triplet A with the absorption coefficient a_{\parallel} for E parallel to the reorienting stress larger than α_{\perp} for **E** perpendicular to that same stress. Now, the total dichroism at 8 K is due to atomic reorientation of the center as well as to electronic reorientation. One kind of stress-induced electronic reorientation of centers implies selective trapping of previously thermalized carriers at centers where the stress-dependent binding energy of the carriers is the largest and this is the one expected for an O-V center.⁵ If only one charge state of the center exists, at the end, one carrier will bind to each center whatever the binding energy and no net effect will result. Hence, the absence of dichroism in this case could indicate that no atomic reorientation takes place for our experimental conditions and then that the dichroism observed for the other sample is an electronic effect. This absence of atomic dichroism, which has to be confirmed, could be related to the change in energy with strain of the Ga-O-Ga chain compared to that of the Ga-Ga reconstructed bond. Now, these two bonds lie in perpendicular planes; if the energy change with strain is nearly the same for the two bonds and if they both minimize their energy under stress by orienting in the same way, the magnitude of the stress-induced dichroism of the center will depend on the difference between the particular reorientation energies. If this difference is small, no appreciable atomic reorientation of the Ga-O-Ga dipole is expected. Finally, we would

- *Permanent address: Institute of Semiconductors of the Chinese Academy of Sciences, Beijing, China.
- ¹Z. L. Akkerman, L. A. Borisova, and A. F. Kravchenko, Fiz. Tekh. Poluprovodn. **10**, 997 (1976) [Sov. Phys. Semicond. **10**, 590 (1976)].
- ²J. Schneider, B. Dischler, H. Seelewind, P. M. Mooney, J. Lagowski, M. Matsui, D. R. Beard, and R. C. Newman, Appl. Phys. Lett. **54**, 1442 (1989).
- ³C. Song, B. Pajot, and F. Gendron, J. Appl. Phys. (to be published).
- ⁴H. Ch. Alt, Appl. Phys. Lett. 55, 2736 (1989).
- ⁵G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001

like to point out that the coefficients A_i for $O-V^0$ in silicon and for $O-V_{As}$ in GaAs given in Table I are not very different; however, before drawing conclusions from this on the charge state of the center, comparison with the coefficients A_i of centers B and C must be obtained.

Inversely, under the same conditions, optical dichroism was observed for O_i . This indicates that detectable atomic reorientation of O_i already takes place near ambient in GaAs and further experiments are underway to obtain a spectroscopical value of the diffusion coefficient of O_i in GaAs near room temperature as this was done in Ref. 11 for silicon and germanium.

The material was kindly provided by Y. Wang and B. Ma and we thank M. Lemal for the orientation and cutting of the samples.

(1961).

- ⁶J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).
- ⁷A. A. Kaplyanskii, Opt. Spectrosc. 16, 329 (1964).
- ⁸D. R. Bosomworth, W. Hayes, R. L. Spray, and G. D. Watkins, Proc. R. Soc. London Ser. A **317**, 133 (1970).
- ⁹H. R. Chandrasekhar, P. Fisher, A. K. Ramdas, and S. Rodriguez, Phys. Lett. **41A**, 137 (1972).
- ¹⁰The piezospectroscopy of O_i in silicon was reported in Ref. 8 for a maximum stress of about 350 MPa.
- ¹¹J. W. Corbett, R. S. McDonald, and G. D. Watkins, J. Phys. Chem. Solids **25**, 873 (1964).