Local-Vibrational-Mode Spectroscopy of DX Centers in Si-Doped GaAs under Hydrostatic Pressure

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We report the observation of a new local vibrational mode (LVM) in hydrostatically stressed, Si-doped GaAs. The corresponding infrared absorption peak is distinct from the Si_{Ga} shallow-donor LVM peak and is assigned to the Si DX center. The relative intensities of the Si DX LVM and the Si shallow-donor LVM peaks and photoquenching behavior of the sample are consistent with the appearance of a defect which binds two electrons as it undergoes a large lattice relaxation at approximately 23 kbar.

Si is a shallow donor in GaAs and $Al_xGa_{1-x}As$ ($x < 0.22$) when it occupies a Ga site (Si_{Ga}). However, there is another atomic configuration, referred to as a DX center, in which the lattice relaxes in the neighborhood of the Si atom.[1] In contrast to substitutional Si, the Si DX center is a deep-level defect which is characterized by several unusual physical properties, including a large Stokes shift[2] (1.1 eV) and persistent photoconductivity.[2] It has been[3,4] observed in $Al_xGa_{1-x}As$ for $x > 0.22$ and GaAs under hydrostatic pressure[5] of greater than roughly 20 kbar. Under such conditions of alloying or pressure, or combinations of the two, the DX center becomes more stable than the shallow donor and the shallow donors transform into DX centers. The mechanism for this transformation is not yet fully understood, but it has been recently suggested that it occurs via an intermediate excited state.[6,7] Similar behavior is seen for many other donor atoms. While a great deal of progress has been made in the understanding of the DX center, e.g., confirming that the shallow-deep transition is related to changes in the structure of the conduction band,[5] the charge state of the defect is still the subject of controversy.

A recent theoretical model[8,9] proposed to explain the behavior of DX centers suggests that this defect is a negative-U center.[10] This implies that, although the impurity is only singly, positively charged, its energy is lower when it binds two electrons rather than one. A lattice relaxation accompanies the localization of the second electron, and the decrease in energy caused by this relaxation is sufficient to overcome the additional Coulomb repulsion. Similar models have been used to describe interstitial boron[11] in Si and an oxygen-arsenic vacancy complex in GaAs,[12] both of which have been found to exhibit negative-U behavior.

Most, but not all, experiments testing the validity of the negative-U model for the DX center have either supported the model or been inconclusive. A recent experiment using deep-level transient spectroscopy on samples codoped with germanium and silicon found that DX centers associated with the Ge atoms bound two electrons,[13] and Mössbauer measurements on Sn-doped GaAs have been interpreted as showing that two or three electrons are localized at each DX center.[14] Recent interpretations of thermal capture and emission kinetics data of DX centers have been shown to be consistent with a negatively charged DX center, but not with a neutral DX center.[15,16] Studies of the change in mobility caused by a DX transformation should also help determine if these defects are charged or neutral, but the interpretation of existing data has not led to definitive conclusions.[17–19] One experiment which is in conflict with the negative-U model used magnetic-susceptibility measurements to show that DX centers in several approximately 10-μm-thick epilayers of $Al_xGa_{1-x}As$ ($x > 0.23$) doped with Si or Te were paramagnetic, implying that only one electron was bound.[20] However, a similar experiment performed on a 200-μm-thick epilayer of $Al_{0.3}Ga_{0.7}As$:Te which had its substrate removed found that the concentration of paramagnetic centers was an order of magnitude less than the concentration of DX centers.[21]

In this Letter, we report the first use of a well established technique, far-infrared Fourier-transform spectroscopy (FIRFTS) of local vibrational modes, to study the Si DX center in GaAs. Spectroscopy of local vibrational modes (LVMs) has been extensively used for studying defects in semiconductors,[22] but this technique has not been previously used to study the DX center for the following reasons. If one wishes to perform experiments without applying pressure, alloys must be used. However, the vibrational spectra of alloys are extremely difficult to interpret because variations in the local environment of the defect lead to substantial broadening of LVM peaks. If pressure is employed to avoid the use of alloyed samples, then the sample must be placed in a diamond-anvil cell (DAC). This is one of the only tools available for achieving the high pressures necessary in a cell which allows optical access. Unfortunately, this lim-

its sample size to the order of a few hundred micrometers in diameter and roughly 100 μm in thickness. While it is common practice to do spectroscopy in a DAC on samples where the absorption is due to intrinsic effects (i.e., 10^{22} atoms/cm^3), spectroscopy of defects, where typical concentrations are 10^{17}-10^{18} cm^{-3}, has not been successfully performed to our knowledge. The problem is one of achieving a sufficient signal-to-noise ratio.

This Letter describes the observation of the Si LVM in GaAs under large hydrostatic pressure. All spectra were recorded with a Digilab FTS-80 Fourier-transform spectrometer. The diamond-anvil cell, which has been previously described by its developers,[23] was mounted in a Janice Super VP cryostat. A Ge:Be photoconductor, which has a photoconductive onset at 200 cm^{-1}, was used as the detector.[24] To increase signal-to-noise ratio, a cone was used to concentrate light on the cell and the detector was mounted directly behind the cell in an integrating optical cavity. The samples were cylinders of GaAs:Si 300 μm in diameter and approximately 100 μm thick. The pressure medium used was a 4:1 mixture of methanol and ethanol. This mixture has been shown to be hydrostatic[25] up to 100 kbar, well above the pressures used for this work. The ruby fluorescence method[26,27] was used to measure the pressure in the cell.

The Si_{Ga} vibrational mode occurs at 384 cm^{-1} at zero pressure.[28] In order to determine if some change in the LVM occurs upon transforming into a DX center, it is first necessary to determine where the mode of the untransformed center lies under pressure. This was done
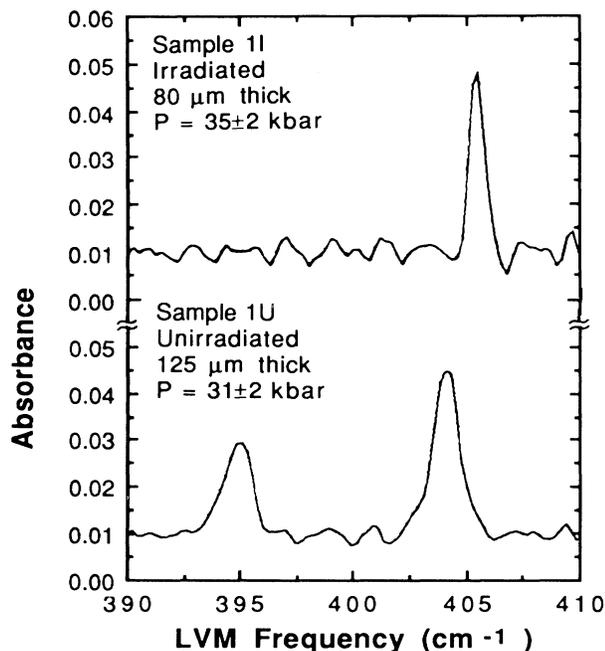
using a piece of GaAs:Si with $n = 6.3 \times 10^{17}$ cm^{-3}, subsequently referred to as sample 1I. This sample had been irradiated, resulting in its being transparent to infrared radiation at all pressures.[29] A transformation of the Si shallow donor to a Si DX deep donor cannot take place in this sample since there are no longer any free electrons available. A spectrum of sample 1I in the DAC taken at $P = 35 \pm 2$ kbar is shown in Fig. 1, and the dependence of the LVM frequency on pressure is shown in Fig. 2. The dependence is linear, and the change in frequency with pressure is $dv_{Si_{Ga}}/dp = 0.66 \pm 0.03$ cm^{-1}/kbar.

Figure 1 also shows the spectrum of sample 1U at 30 ± 2 kbar, which is well above the pressure necessary to cause the DX transformation. This sample is identical to sample 1I, having been cut from the same wafer, except that it had not been irradiated. There are two peaks clearly observed in the spectrum, one at 404 cm^{-1} and the other at 395 cm^{-1}. The peak at 404 cm^{-1} is precisely where the Si_{Ga} LVM is expected at 31.5 kbar, but the peak at 395 cm^{-1} is a new feature. The pressure dependence of this new feature is shown in Fig. 2 and is $dv/dp = 0.61 \pm 0.04$ cm^{-1}/kbar, roughly the same as that of the Si_{Ga} peak. This new feature will be identified as the LVM of the Si DX center.

As a first step in making this identification, we confirmed that DX centers were present in the sample by performing the following two experiments. First, the sample was illuminated with white light while at 4 K. The amount of light reaching the detector was drastically reduced because of free-carrier absorption resulting from the persistent photoconductivity of the DX centers,
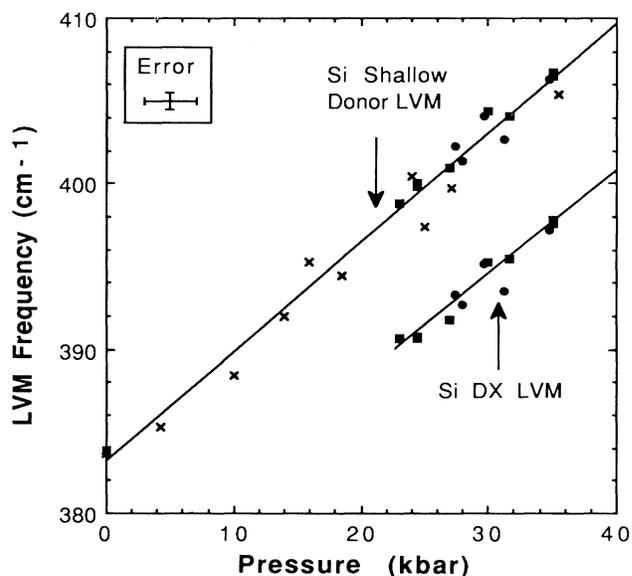

FIG. 1. Absorption spectra of samples 1I and 1U at $T = 5$ K.

FIG. 2. Pressure dependence of the Si_{Ga} and Si_{DX} LVM frequencies. $\times$, $\bullet$, and $\blacksquare$ refer to samples 1I, 1U, and 2, respectively.

and an absorption spectrum of the sample could no longer be taken. Second, the sample was brought to room temperature and recooled at a pressure of only 21 kbar, too low to cause the DX transformation. Once again, no spectrum of the sample could be taken. Bringing the sample back to room temperature and increasing the pressure to 24 kbar resulted in the sample once again being transparent.

In heavily doped GaAs:Si samples, many LVM peaks in addition to the Si_{Ga} peak have been observed with FIRFTS.[28] They can be assigned to $^{28}Si_{As}$, $^{28}Si_{Ga}$-$^{28}Si_{As}$, Si-X, Si-Y, $^{29}Si_{As}$, and $^{30}Si_{As}$. We exclude the possibility that the lower-frequency peak we observe is due to any of the defects listed above based on the results of the following experiment. A bulk piece of sample 1I was investigated by conventional absorption spectroscopy at zero pressure, and the only observable peak was that due to $^{28}Si_{Ga}$. This is consistent with the fact that only one peak was observed when sample 1I was in the DAC, but provides a more stringent test since the signal-to-noise ratio for conventional spectroscopy is far superior to spectroscopy performed in the DAC. As an additional check, if we extrapolate the frequency of the new peak to zero pressure, it would be found at 376 ± 1.5 cm^{-1}. This value lies between the frequencies of the ^{29}Si and ^{30}Si LVM peaks reported in Ref. 25, and the absorbance in these peaks is less than 10% of the absorbance due to $^{28}Si_{Ga}$. In contrast, the new LVM peak we observe has roughly half the absorbance of the $^{28}Si_{Ga}$ LVM peak. The above arguments demonstrate conclusively that the lower-frequency LVM is due to a previously unobserved defect which is only formed by the application of pressure in a sample where free electrons are available. We therefore identify this new peak as the LVM of the Si DX center.

In order to use our spectroscopic data to determine the charge state of the DX center, it is necessary to know the compensation ratio in our samples. The compensation ratio θ, which is the ratio of the concentration of ionized acceptors to ionized donors, can be determined from values of the low-temperature mobility and concentration.[30] These data were obtained by Hall-effect measurements and are displayed in Table I along with the results of our calculations. Our analysis took into account the concentration dependence of the effective mass of the electron.[31]

We now use the collected data to infer the charge

state of the DX center. Since the area of the Si_{Ga} LVM peak observed in spectra of sample 1I is equal to within 30% to the sum of the areas of the Si_{Ga} and the Si_{DX} LVM peaks seen in spectra of sample 1U, we conclude that the cross section for LVM absorption by these two defects is the same to within this accuracy. Knowing the relationship between the cross sections of the two defects allows us to use the compensation ratio to predict the ratio of the peak areas $A_{Si_{Ga}}/A_{Si_{DX}}$ observed for a given sample. Since the cross sections are equal to within our specified error, we have $A_{Si_{Ga}}/A_{Si_{DX}} = n_{Si_{Ga}}/n_{Si_{DX}}$, where n is the concentration of the corresponding defect. The theoretical ratio $n_{Si_{Ga}}/n_{Si_{DX}}$ depends on the compensation in the sample and the charge state which is assumed for the DX center. If the DX center were a neutral defect, all uncompensated donors should undergo the DX transformation and the ratio of the concentration of Si shallow donors to Si DX centers would be $n_{Si_{Ga}}/n_{Si_{DX}} = \theta/(1-\theta)$. If the DX center were negatively charged, the concentrations would be related to the compensation ratio by $n_{Si_{Ga}}/n_{Si_{DX}} = (1+\theta)/(1-\theta)$. A comparison between our experimental data and the predictions for a neutral and a negatively charged DX center is shown in Fig. 3. The data clearly support the negatively charged DX center.

Since there is not complete agreement between different sources on obtaining compensation ratios from concentration and mobility data, we consider how using theories other than the one chosen here would affect the interpretation of the data. Any model which includes scattering effects other than those considered in Ref. 30 would lead to lower compensation ratios, and would therefore shift the data points even further away from the DX^0 curve shown in Fig. 3. A recent model[32] which claims that screening effects in other models have been overestimated also leads to lower compensation ratios. It therefore appears that using other models would not change our conclusion that the DX center is negatively charged.

TABLE I. Results from Hall-effect analysis.

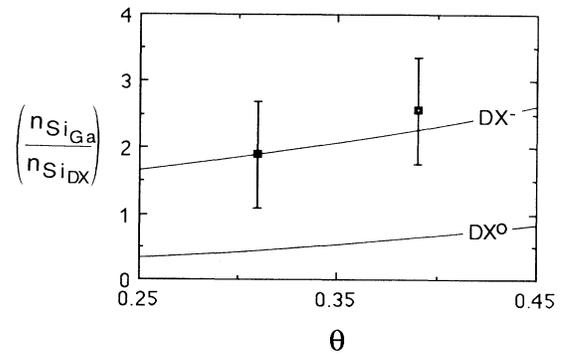| Sample	$N_D - N_A$ (10^{18} cm^{-3})	$\mu_{110 K}$ (10^3 cm^2/V s)	θ
1I	0.63	$\cdots$	$\cdots$
1U	0.63	2.70	0.31
2	2.9	1.53	0.39

FIG. 3. Comparison between experimental results and theoretical predictions for the ratio $n_{Si_{Ga}}/n_{Si_{DX}}$ as a function of compensation.

We now discuss the consistency of our results with other experimental and theoretical work. In Ref. 4, data describing electron capture at DX centers are used to imply that they should have an LVM at a frequency much lower (< 80 cm^{-1}) than the frequency of the DX center LVM we observe. Our work does not exclude the existence of such a mode since our detector was not sensitive to light at these low frequencies. Also, if the negative-U model proposed in Refs. 7 and 8 is correct, the Si substitutional donor transforms into a DX center by breaking a bond with one of the nearest-neighbor arsenic atoms and moving into an interstitial position. It is therefore intriguing that the LVM frequency of the DX center is so close to that of the unperturbed donor. However, since the lattice relaxation proposed in this model involves changes in the Si-As nearest-neighbor bond lengths and bond angles, accurate LVM frequencies of the new configuration are difficult to predict.

In conclusion, the LVM of the Si DX center in GaAs has been observed for the first time. The shift of the LVM frequency with pressure was found to be $d\nu_{\text{Si}_{DX}}/dp = 0.61 \pm 0.04$ cm^{-1}/kbar for the Si DX center and $d\nu_{\text{Si}_{\text{Ga}}}/dp = 0.66 \pm 0.03$ cm^{-1}/kbar for Si$_{\text{Ga}}$. The ratio of the area of the Si$_{\text{Ga}}$ absorption peak to that of the Si DX absorption peak has been combined with Hall-effect analysis to provide further evidence supporting the negative-U model for the DX center.

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