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Temperature-dependent changes on the sulfur-passivated GaAs (111)*A*, (100), and (111)*B* surfaces

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The chemical bonding changes as a function of temperature in sulfur-passivated GaAs (111)*A*, (100), and (111)*B* surfaces were monitored *in situ* by synchrotron-radiation photoelectron spectroscopy. At relatively low temperatures ($T \cong 200\,^{\circ}\mathrm{C}$), As—S bonds are converted to Ga—S bonds. At higher temperatures, a well-ordered monolayer is observed and a predesorption state is observed for both the (111)*A* and (111)*B* surfaces at about 50 °C below the S desorption temperature for the respective surfaces. It is also found that the S desorption temperature is well correlated with the coordination number of the sulfur atom on the GaAs surface.

I. INTRODUCTION

While GaAs appears to be an excellent candidate for a variety of electronic devices, commercial development of GaAs technology has been hampered by the existence of surface states and pinning of the Fermi level near the midgap. It is generally recognized that a reduction of surface states is necessary not only for the fabrication of GaAs electronic devices, but also to help elucidate the Fermi-level pinning mechanism on the GaAs surface.[1–4]

Sandroff's reported current-gain enhancement of GaAs/$\mathrm{Al}_{1-x}\mathrm{Ga}_x\mathrm{As}$ heterostructure bipolar transistors by $\mathrm{Na}_2\mathrm{S}$ chemical treatment[5] in 1987 spurred interest in passivating the GaAs surface by wet chemical means. However, the reported gains made by using this treatment have been shown to be a result of band bending and not surface-state reduction.[6,7] Nevertheless, wet chemical S passivation of GaAs surfaces spurred others into trying to improve on this passivation technique. One promising candidate is the $(\mathrm{NH}_4)_2\mathrm{S}_x$ passivation treatment.[8] This treatment has been shown to significantly reduce the surface-state density.[9,10] Furthermore, metals deposited on this passivated surface have been shown to produce Schottky barrier heights which vary as the work function of the deposited metal indicating that the GaAs surface is unpinned in the treated state.[11,12] Additional advantages include good cleaning of the GaAs surface oxides and nearly complete S coverage.[8] Furthermore, this treatment is quite stable with time.

However, the wet chemical treatment alone is not sufficient in preparing a well-ordered monolayer S-passivated GaAs surface, which is of interest in the fabrication of 3D GaAs electronic devices. In order to prepare such surfaces, the sample must be placed in vacuum where a sulfur residue of approximately 100 Å quickly sublimes at room temperature (RT) followed by sample heating in the 300 °C–500 °C range where the S monolayer becomes well ordered. The thermal-dependent behavior for the GaAs (111)*A*, 100, and (111)*B* surfaces is the primary focus of this investigation.

II. EXPERIMENT

The samples were *n*-type GaAs wafers (Si doped) with a carrier density of 1×10^{18} cm^{-3}. The GaAs wafers were treated with a $(\mathrm{NH}_4)_2\mathrm{S}_x$, $x=3$ solution for 1 h at 60 °C.

The S-treated samples were then placed in a combined surface analysis system[13] which is located at Photon Factory beam line BL-1A in Tsukuba. The photon energy was adjusted to 210 eV using a grating/crystal monochromator[14] with a 1200 lines /mm grating to obtain surface sensitive information on the S 2*p* core levels. The incident photon energy calibration was made by recording the kinetic energy of the Au 4*f* levels. In addition, x-ray photoemission spectroscopy (XPS) (Al *Kα*) was also performed to confirm core-level shifts, although the surface sensitivity of the XPS measurements were not as good as the synchrotron-radiation photoelectron spectroscopy (SRPES) measurements. In addition, surface structures were also measured by low-energy electron diffraction (LEED).

The temperature of the sample during heating was measured by an optical pyrometer. Two different heating procedures were employed. In the first procedure, the sample was slowly heated from RT to the S desorption temperature of the particular surface. In the second procedure, the sample was heated more quickly by applying a resistive current in steps starting from 3.0 to 6.0 A in 0.25-A steps. In both cases, the general spectral characteristics were the same for both procedures.

III. RESULTS AND DISCUSSION

A. S/GaAs (111)*A*

The SRPES S 2*p* spectra for S/GaAs(111)*A* is shown as a function of temperature in Fig. 1. At room temperature, there are essentially two peaks centered at binding energies of 162.3 and 163.4 eV, which correspond to Ga—S and As—S bonds, respectively.[15] As the tempera-

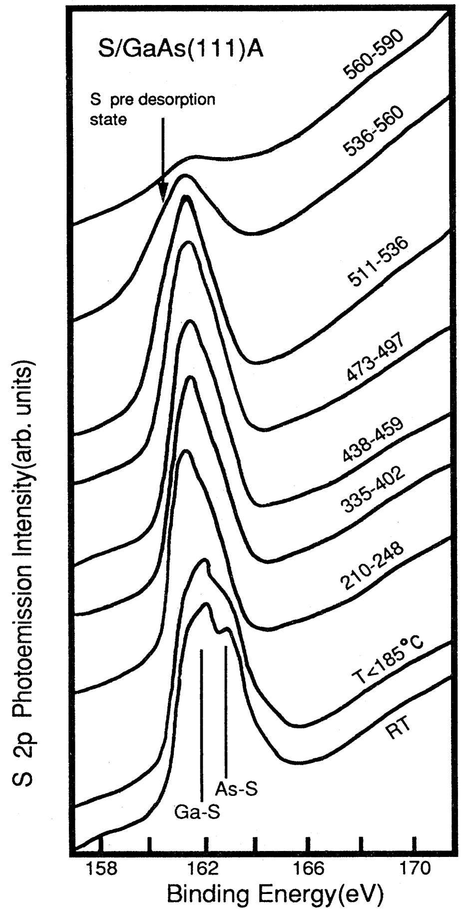

FIG. 1. The SRPES S 2*p* spectra are shown for temperatures ranging from room temperature (RT) to the desorption temperature ($T_D \cong 586\,^\circ\mathrm{C}$) for the S/GaAs (111)*A* surface.

ture is raised, the intensity of the Ga—S bond increases at the expense of the As-S intensity. Integration of the peak area gives nearly the same area for the RT S 2*p* and heated S 2*p* areas indicating that a As-S to Ga-S conversion takes place as the S/GaAs sample is heated. One can also see from Fig. 1 that most of the As-S to Ga-S exchange takes place at reasonably modest temperatures ($T \cong 200\,^\circ\mathrm{C}$).

The importance of this exchange is due to the fact that the As-S antibonding state is occupied to a certain extent and lies within the GaAs band gap and is thus a GaAs surface state.[16] However, the Ga-S antibonding state lies above the GaAs conduction band and is unoccupied while the Ga-S bonding state lies well within the GaAs valence band. Thus this As-S–to–Ga-S exchange means a reduction of surface states and unpinning of the GaAs surface. This has been shown experimentally by *C-V* measurements of the surface density of states[9,10] and metal-dependent Schottky barrier heights deposited on sulfur-passivated GaAs.[12] The driving force for this exchange reaction is rationalized by the greater heat of formation of Ga-S with respect to As-S (Refs. 17 and 18) as well as the greater ionicity of Ga-S and bond energy with respect to As-S.[16]

At a temperature of 545 °C, the low binding energy (BE) side of the Ga-S peak grows larger in intensity. Curve deconvolution indicates this peak is located at 160.6 eV (the Ga-S main peak is located at 161.6 eV). This peak occurs on the lower binding energy side of the Ga-S peak suggesting a significant electron charge transfer from Ga to S prior to desorption. Furthermore, this peak disappears with complete desorption of sulfur suggesting the origin of this peak cannot be attributed to a state from the GaAs substrate. Based on the relation between the S formal charge and the S 2*p* XPS core-level shift,[19] this 1-eV shift roughly corresponds to a S^{-1} state where the charge transfer takes place from Ga to S. The nature of this peak is not yet clearly understood, but it may be related to the formation of a predesorption state and the onset of S desorption. It is interesting to note that Melloch *et al.*[20] observe a dramatic change in the reflection high-energy electron diffraction (RHEED) pattern (twofold reconstruction) at 530 °C for the S/GaAs (110) surface prior to additional (fourfold) reconstruction that takes place above 580 °C. This result seems to corroborate our findings in that at about 50 °C below complete desorption, there is a dramatic change in the treated GaAs surface which we attribute to charge transfer from Ga to S prior to S desorption.

With complete desorption of the surface sulfur species, there is the question as to whether there may exist some embedded S species. One may be led to believe this is the case on the basis of XPS S 2*p* core-level spectra. However, secondary-ion-mass spectroscopy (SIMS) analysis shows that the concentration of S in the GaAs matrix is approximately 4×10^{13} atoms/cm^2 confined to the top 400 Å in the GaAs wafer. This S concentration is too small to contribute to the XPS S 2*p* signal indicating there is essentially no S embedded in the GaAs wafer. The remaining intensity in XPS Al *Kα* excited S 2*p* spectra is from the Ga 3*s* core peak. On the basis of the mean free path and cross section of Ga 3*s* electrons, one has a mixing of S 2*p* and Ga 3*s* states which does not exist for the 210-eV photon energy used in the SRPES S 2*p* spectra.[21,22] Finally, additional precise measurement gives a value of 586 °C for the S desorption temperature on the (111)*A* surface.

B. S/GaAs (100)

The SRPES S 2*p* spectra for the S/GaAs (100) system is plotted in Fig. 2. Again one can see that as the temperature of the sample is raised, the S bonds more preferentially with the Ga atoms on the GaAs surface. However, in contrast to the (111)*A* and (111)*B* surface, no low BE S state is observed prior to S desorption. This however does not mean that this state may exist since it was found that the strength of this state depends on how quickly the sample is heated and may depend on other sensitive heating parameters. One may also note that the desorption temperature for the (100) surface appears to be lower than the (111)*A* surface. This is however due to poor heating control in this temperature region for this sample.

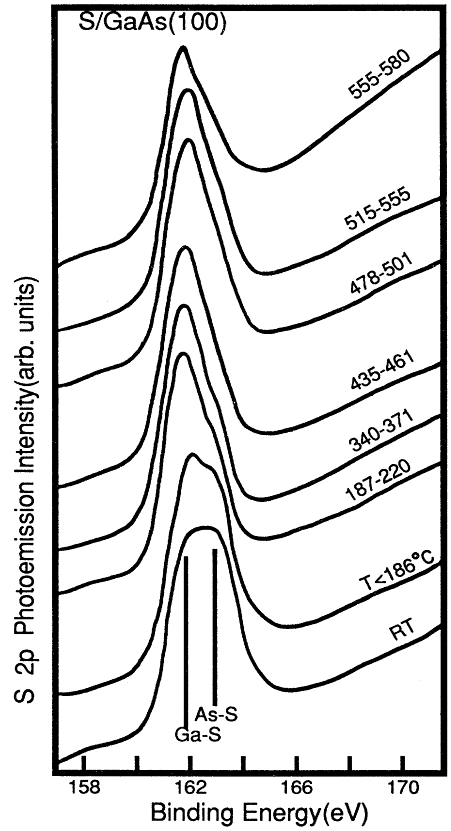

FIG. 2. The SRPES S 2p spectra are shown for temperatures ranging from room temperature (RT) to the desorption temperature ($T_D \cong 596\,^{\circ}\mathrm{C}$) for the S/GaAs (100) surface.

Additional more precise measurements were made and a desorption temperature of 596 °C was found for this surface. For the (100) surface, a 4×1 LEED pattern was observed which is similar to the LEED pattern for the clean unpassivated surface. This result suggests that there is little or no reconstruction after S desorption.

C. S/GaAs (111)*B*

The SRPES S 2p spectra for the S/GaAs (100) system is plotted in Fig. 3. As in the case of the (111)*A* and (100) surfaces, S preferentially bonds with the Ga atoms on the GaAs surface as the temperature is raised. Similar to the (111)*A* surface, low BE S states are observed prior to S desorption for the (111)*B* surface. Spectral deconvolution indicates two low-energy peaks at 160.10 and 159.10 eV which correspond to S^{-1} and S^{-2} states, respectively. One can also see that the As-S–to–Ga-S intensity ratio is higher at RT for the (111)*B* surface than the (111)*A* surface as expected since the (111)*B* surface is As exposed while the (111)*A* surface is Ga exposed. This is discussed in more detail in the following section.

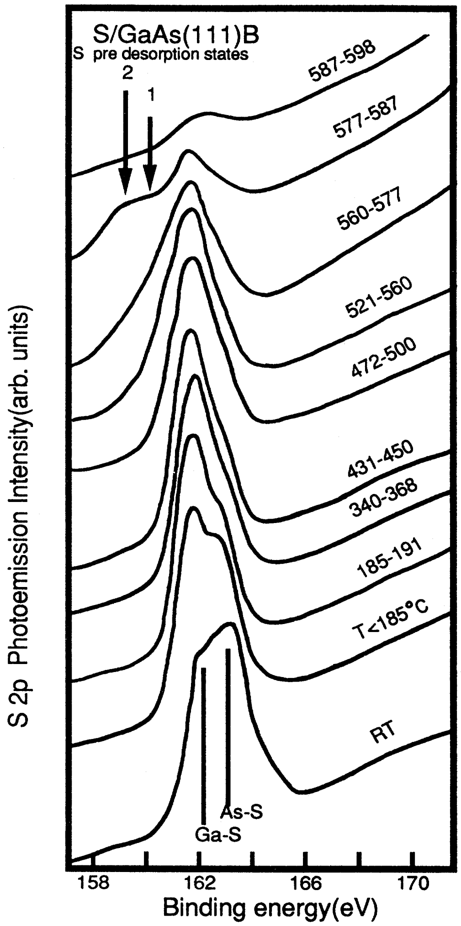

FIG. 3. The SRPES S 2p spectra are shown for temperatures ranging from room temperature (RT) to the desorption temperature ($T_D \cong 618\,^{\circ}\mathrm{C}$) for the S/GaAs (111)*B* surface.

Finally a S desorption temperature of 618 °C was determined indicating that with respect to sulfur, the S/GaAs (111)*B* surface is the most stable of the three surfaces studied here. After cooling the S desorbed sample, a 1×1 LEED pattern was observed which is similar to the LEED pattern observed for S/GaAs (111)*B* when it is annealed at 480 °C for 10 min. Further, a 1×1 LEED pattern is observed for the clean unpassivated (111)*B* surface. These LEED results suggest that, similar to the (100) case, there is little or no reconstruction on the (111)*B* surface during S desorption.

D. Spectral comparisons

An interesting aspect seen during the course of this experiment concerned the poor reproducibility in the SRPES S 2p spectral shape after the sulfur-treated sample was placed in vacuum and measured without heating the sample. In Fig. 4(a) are shown three S 2p spectra run without sample heating for S/GaAs (111)*B* surface. One can clearly see that the As-S–to–Ga-S intensity ratios for the three different samples are clearly different. Further-

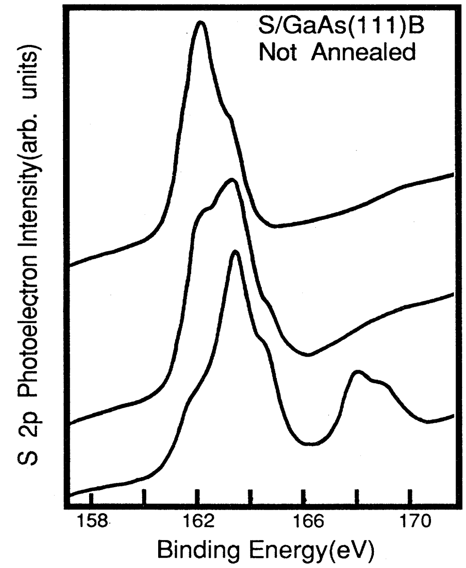

FIG. 4. The SRPES S 2*p* spectra are shown at RT for the S/GaAs (111)*A* surface. The spectral differences are ascribed to slight changes in the sample preparation procedure. After annealing the samples, Ga-S becomes dominant at the expense of As-S bonding. Furthermore, the spectral differences between the three different samples essentially disappear.

more, there is a large peak at 168 eV. This peak is assigned to a S electropositive species. There was a similar peak observed for the S/GaAs (111)*A* surface that came from the sample batch that was S, which suggests that this peak may be a result of this treatment. Furthermore, no similar high BE peaks were observed for the Ga or As 3*d* spectra indicating that this species exists on the surface of the S layer. XPS S 2*p* measurements also confirm that this is a surface species since the peak exists, but with much reduced intensity, as one would expect based on the cross-section and mean-free-path differences between SR and XPS S 2*p* electrons.[21,22] A likely candidate for this species is (SO_x) since the BE shift is consistent with a S—O bond[19] and is probably formed by reacting with trace but variable amounts of water vapor in the atmosphere. These results show that there is considerable variability in the S bonding on the GaAs surface prior to annealing.

However, as mentioned above, the Ga-S is more stable than the As—S bond indicating that the eventual conversion of As-S to Ga-S is thermodynamically controlled and thus any spectral differences essentially disappear when the passivated samples are heated and conversion of As-S to Ga-S bonding takes place. Moreover, the high BE S 2*p* peak essentially disappears and coincides with a significant reduction in the intensity in the O 1*s* region, further strengthing the argument that the S 2*p* high BE peak is a SO_x species that is driven off by heating the sample. Finally, these results suggest that while there is a considerable amount of variability in the nature of the S monolayer GaAs surface prior to annealing, a reproducible S/GaAs surface is produced after annealing.

Another interesting feature is shown in Fig. 5(a) which shows the SRPES S 2*p* spectra for the S/GaAs (111)*A*, 100, and (111)*B* surfaces at RT. One can see that there are large systematic spectral differences between the three S 2*p* spectra for the three surfaces. In particular, the As-S-to-Ga-S ratio is lowest for the Ga exposed (111)*A* surface and is highest for the As exposed (111)*B* surface as expected. On annealing the three samples, the large spectral differences disappear, as shown in Fig. 5(b).

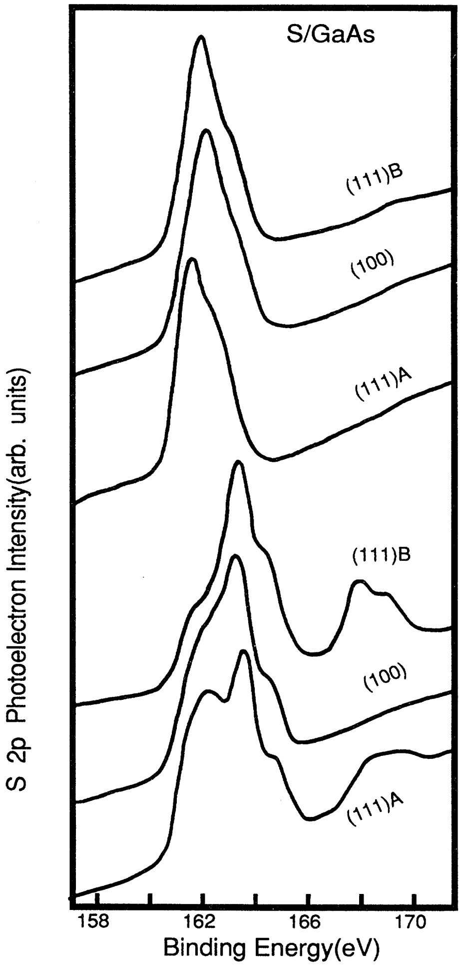

FIG. 5. The SRPES S 2*p* spectra are shown before (lower three figures) and after (top three figures) annealing for S/GaAs (111)*A*, (100), and (111)*B*.

E. Desorption temperature

One may expect the desorption temperature of sulfur on the three different surfaces to be different based on the idea that the Ga-S coordination number ranges from 1 for the (111)*A* surface to 3 for the (111)*B* surface. To investigate this, desorption measurements were carried out by resistively heating the sample in increments of 0.25 A every 5 min starting from 3.0 A and ending at 6.0 A. The experiment was done so that the temperature was recorded while the S 2*p* spectra were taken. The desorption data is shown in Fig. 6. The curves are not a best fit to the data but simply aid in visualizing the differences be-

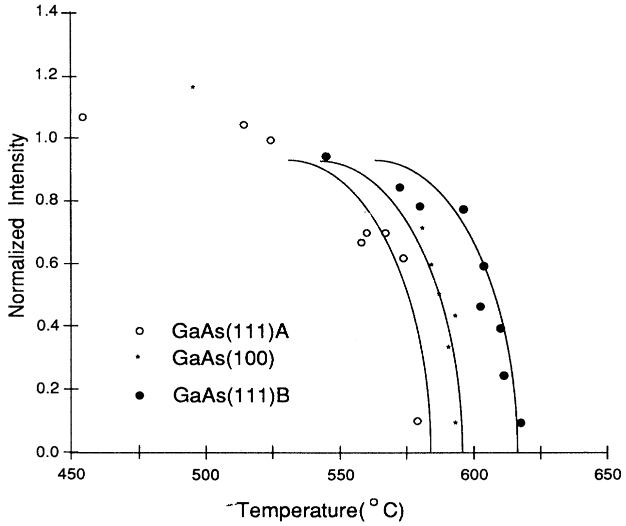

FIG. 6. The SRPES S 2*p* peak intensity is plotted as a function of sample temperature for the S/GaAs (111)*A*, (100), and (111)*B* surfaces. The desorption temperatures for the three surfaces are 586 °C, 596 °C, and 618 °C, respectively.

tween the three desorption cases. One can clearly see that there are significant differences between the three surfaces with the S/GaAs (111)*A* surface being the most unstable while the S/GaAs (111)*B* is the most stable surface. The temperature at which the S completely disappeared was 586 °C, 596 °C, and 618 °C for the (111)*A*, 100, and (111)*B* surfaces, respectively. The number of Ga—S bonds is plotted against the desorption temperature in Fig. 7, illustrating the good correlation between T_D and the sulfur coordination number.

The desorption temperature should also be a rough indicator of the S—Ga bond strength. Recently, Ohno[16,23] performed first-principles band-structure calculations for these three different surfaces and obtained a S-Ga binding energy of 4.3, 5.6, and 6.1 eV for the (111)*A*, 100, and (111)*B* surfaces respectively. This is in good accord with the experimental desorption temperatures, as expected.

IV. CONCLUSIONS

The S 2*p* spectra exhibit chemical bonding and structural changes as the temperature of the different S/GaAs systems is raised. At low temperatures, there is an exchange reaction taking place as sulfur, which bonds to a certain extent to As, bonds almost exclusively with Ga regardless of the surface. A low BE S state was also found at a temperature just below the desorption temperature for the (111)*A* and (111)*B* surfaces which was attributed to a predesorption state. It was also found that the S/GaAs surface for a particular crystal face strongly depends on the sample preparation and is not particularly reproducible. However, the surface does attain a similar state when the sample temperature is raised and the As-Ga exchange reaction can take place. Many of the large spectral differences between the three different crystal faces were also diminished to a great extent when the sample was heated. Finally, the sample desorption temperature was also found to correlate quite well to the sulfur coordination number and the Ga-S theoretical binding energy on the GaAs surface indicating that the (111)*A* is the most unstable S-passivated surface while the (111)*B* S-passivated surface was found to be the most stable.

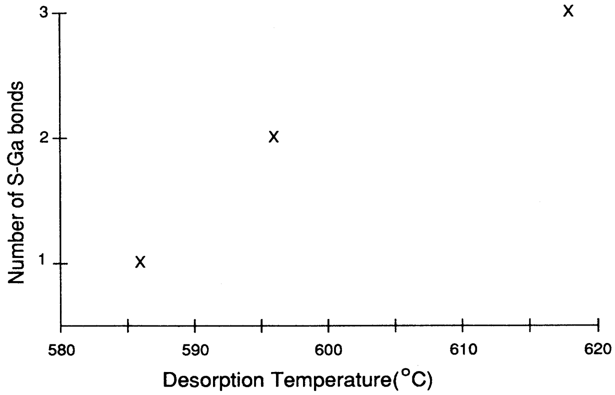

FIG. 7. The number of S—Ga bonds on the S/GaAs surface is plotted against the desorption temperature for the (111)*A*, (100), and (111)*B* surfaces. In this case the (111)*A*, (100), and (111)*B* have one, two, and three Ga—S bonds, respectively.

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