

Sulfur Structural and Chemical Bonding Changes for Metal/S-Passivated GaAs(111) Studied by the X-Ray Standing Wave Technique and Synchrotron Radiation Photoemission Spectroscopy

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The interfacial structure and chemical bonding for Al and Pd/S-passivated GaAs were compared to their electrical properties. A well-ordered S interlayer, which was investigated by the X-ray standing wave (XSW) technique, was obtained for Al/S/GaAs(111)B, indicating a higher stability of S-Ga bonds on GaAs(111)B than (111)A. The Schottky barrier height (SBH) for Al/S/GaAs(111)B is slightly lower than that for (111)A. This might be due to the interfacial S layer that is more ordered on (111)B than on (111)A. For Pd/S/GaAs, stable S-Ga bonds on GaAs are easily broken by depositing reactive Pd, and S atoms segregate to the surface for both (111)A and (111)B.

Introduction

Fermi level pinning of the Metal-GaAs interface has been one of the biggest obstacles limiting development of GaAs based devices. Sulfide treatment with $(\text{NH}_4)_2\text{Sx}$ solution was found to be effective as a surface passivation technique for GaAs¹. Evidence for this can be found in the Schottky barrier height (SBH) dependence on metal work function for $(\text{NH}_4)_2\text{Sx}$ -treated GaAs². Although the interfacial structure and chemical bonding for metal/S-passivated GaAs is thought to correlate with their electrical properties, no such correlation has yet been made.

In this study, the S interlayer structure and chemical state after deposition of Al and Pd films on $(\text{NH}_4)_2\text{Sx}$ -treated GaAs(111)A[Ga-terminated surface] and (111)B[As-terminated surface] were investigated by the X-ray standing wave (XSW)^{3,4} technique and Synchrotron Radiation Photoemission Spectroscopy (SRPES). In order to correlate the interface structure with electrical properties, current-voltage (I-V) measurements on Al and Pd/S-passivated GaAs(111)A and (111)B were also performed. Al and Pd have small and large work functions, respectively.

XSW is a highly sensitive method for locating particular atomic species with respect to the substrate lattice unit cell by monitoring secondary emissions from selected target atoms. Using synchrotron radiation soft X-rays, the interfacial structure of light-elements such as sulfur can be analyzed. Photoemission spectroscopy can analyze the chemical bonding. The interfacial structure and chemical bonding

were then correlated with the SBH determined from I-V measurements.

Experiments

Si-doped n-GaAs(111)A and B wafers were used as sample substrates. After chemical cleaning, the GaAs(111) wafers were dipped into an $(\text{NH}_4)_2\text{Sx}$ solution and annealed at 480°C for 10 minutes in vacuum. Al and Pd overlayers were deposited on $(\text{NH}_4)_2\text{Sx}$ -treated GaAs wafers by evaporating from tungsten baskets onto the substrates at room temperature.

XSW and SRPES experiments were carried out at the Photon Factory NTT beam line 1A in Tsukuba. In the XSW experiments, incident soft X-rays 3.0 keV monochromatized by InSb(111) double-crystals were used to excite the substrate (111) standing waves. S $K\alpha$ fluorescence X-rays(2.3keV) generated by the (111) standing waves for the Al and Pd /S/GaAs(111)A and B samples were measured as a function of reflection angle by scanning the sample angle around the (111) Bragg reflection by means of a vacuum goniometer system equipped with a Si(Li) detector⁵. Furthermore, SRPES measurements were also performed for Al deposited S/GaAs(111)A and B samples by a combined surface analysis system⁶. An incident beam with a photon energy of 210eV monochromatized by a 1200g/mm grating was used for obtaining photoemission spectra from the Ga3d and S2p core levels⁷. The SBH for the Al/S/GaAs(111)A and B samples were evaluated from I-V measurements.

Results and Discussion

1. Al/S-passivated GaAs(111)

Figure 1 shows the XSW results of Al/S/GaAs(111). The solid lines represent theoretical fits to the measured reflectivity and S fluorescence yield which are plotted versus the angle relative to the Bragg angle. The best fit to the S fluorescence yields are achieved by assuming a coherent fraction (F) and a coherent position (P) of 0.17 and 0.91 for Al/S/GaAs(111)A. 1.0 and 0.10 are obtained for F and P values of Al/S/GaAs(111)B. A low coherent fraction F value was obtained for GaAs(111)A while a high F value was obtained for (111)B. These results indicate that a S interlayer is completely ordered on GaAs(111)B while S is disordered on GaAs(111)A after Al deposition. This is attributed to the greater stability of the S-Ga bond on GaAs(111)B relative to (111)A⁸. The coherent position P for Al/S-treated GaAs(111)B has nearly the same value as S/GaAs(111)B and CaF₂/S/GaAs(111)B⁹. This means that all S atoms occupy the top layer As atom site for Al/S/GaAs(111)B.

In order to correlate these interfacial structures with the interface chemistry, SRPES was performed on the Al/S/GaAs samples where Al was deposited step by step. Figure 2 shows the SRPES Ga3d and S2p spectra for Al/S/GaAs(111)B sample. Metallic Ga peaks appear in Ga3d spectra for both Al/S/GaAs(111)A and (111)B. Concerning the S 2p spectra, the peak energy moves toward higher binding energy side with Al deposition. The appearance of metallic Ga 3d peaks means that Ga atoms exchange with Al atoms and segregate to the surface. The shift of S 2p peaks can be attributed to chemical shift due to Al-S bond formation or condensation of S atoms at the interface, since there is no shift in Ga3d and As3d spectra due to a band bending effect.

Then, Auger sputtering in-depth profile was measured for Al/S/GaAs(111)B to determine the origin of the S2p chemical shift. As shown in Fig.3, S atoms exist at the interface for both (111)A and (111)B. This indicates that S atoms for both GaAs(111)A and (111)B remain at the Al/S/GaAs(111) interface.

From I-V measurements, a SBH of $\phi_{bn}=0.57\text{eV}$ for Al/S/GaAs(111)B is obtained which is slightly lower than $\phi_{bn}=0.62\text{eV}$ for Al/S/GaAs(111)A. This difference might be attributed to the interface S layer ordered on (111)B compared with (111)A. But even for (111)B, the SBH is far from the Schottky limit of 0.21eV which is simply calculated for the Al/GaAs Schottky contact with an Al work function of 4.28eV and a GaAs electron affinity of 4.07eV. It is thought that the S interlayer on GaAs is not perfectly covered with S atoms and the SBH is influenced by the non-covered region, suggesting that a lower SBH (unpinned)

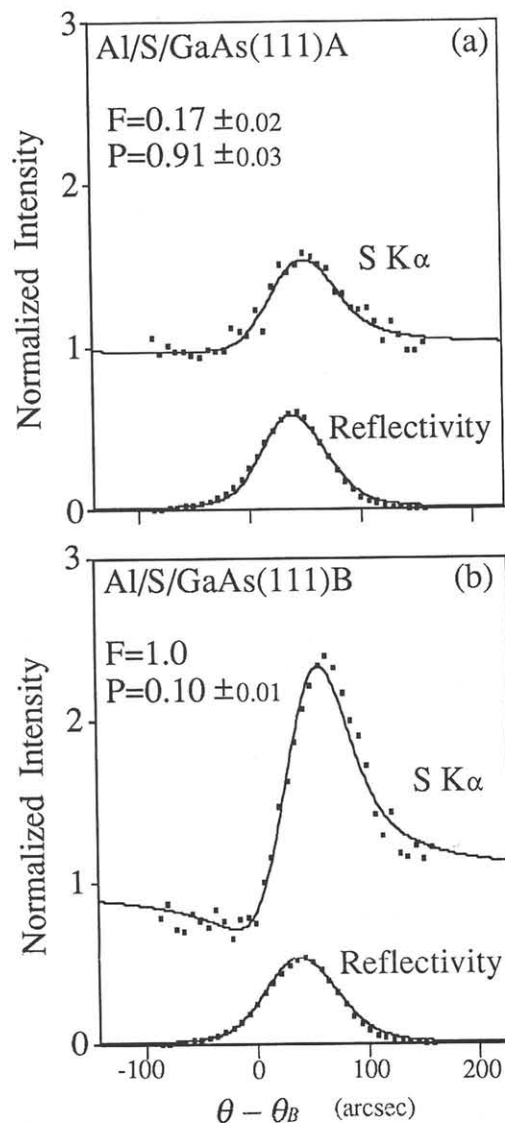


Fig.1 Angle dependence of reflectivity and S K α fluorescence yield near the (111) Bragg condition (a) for Al/S/GaAs(111)A and (b) for Al/S/GaAs(111)B.

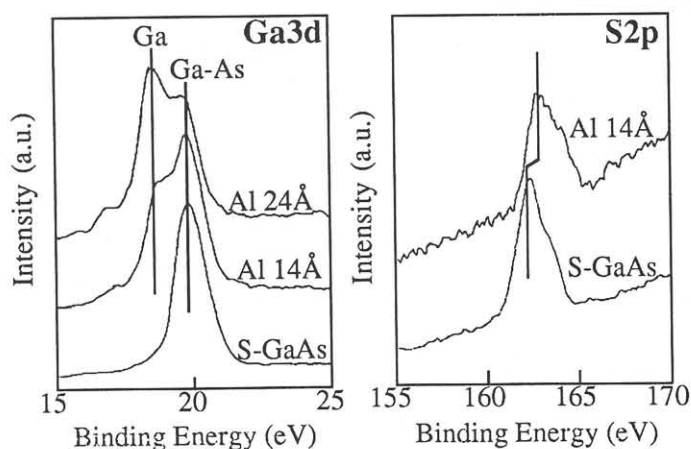


Fig.2 Ga3d and S2p photoemission spectra from Al/S/GaAs(111)B.

Fermi level) may be obtained by completely covering the GaAs surface with S atoms.

2. Pd/S-passivated GaAs(111)

Following this, Pd, which has a large work function (5.12eV), was deposited on S-passivated GaAs(111). XSW profiles of Pd/S/GaAs(111) are shown in fig.4, which are similar to Bragg reflection curve profiles indicating randomly distributed S atoms. Auger sputtering in-depth profiles reveal that S atoms segregate to the surface for both (111)A and (111)B. Stable S-Ga bonds on GaAs are readily broken by depositing very reactive Pd with the subsequent formation of a variety of Pd-GaAs compounds (PdGa, PdAs etc)¹⁰. However, a slightly higher SBH is obtained for Pd/S/GaAs with respect to Pd/GaAs. This may be due to the S layer relaxing the heat of condensation during Pd deposition.

Conclusions

The interfacial structure and chemical bonding for metal/S-passivated GaAs depend on factors including substrate orientation, deposited metal and deposition temperature etc. A well-ordered S interlayer was obtained on Al/S-passivated GaAs(111)B, indicating a higher stability of S-Ga bonds on GaAs(111)B than (111)A. From I-V measurements, the SBH of Al/S/GaAs(111)B ($\phi_{bn}=0.57\text{eV}$) is slightly lower than that of (111)A ($\phi_{bn}=0.62\text{eV}$). For Pd/S/GaAs, stable S-Ga bonds on GaAs are readily ruptured by depositing very reactive Pd. Pd deposition is also accompanied by segregation of S atoms to the surface for both (111)A and (111)B. In order to obtain unpinning Fermi level in metal/S-passivated GaAs systems, a well-ordered interface, suppression of metal-GaAs reaction and a S passivation layer are critical.

References

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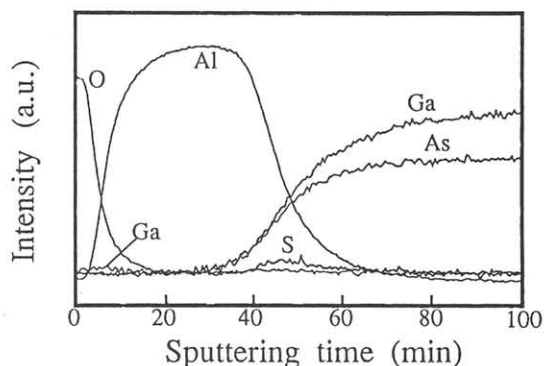


Fig.3 Auger sputtering in-depth profiles for Al/S/GaAs(111)B

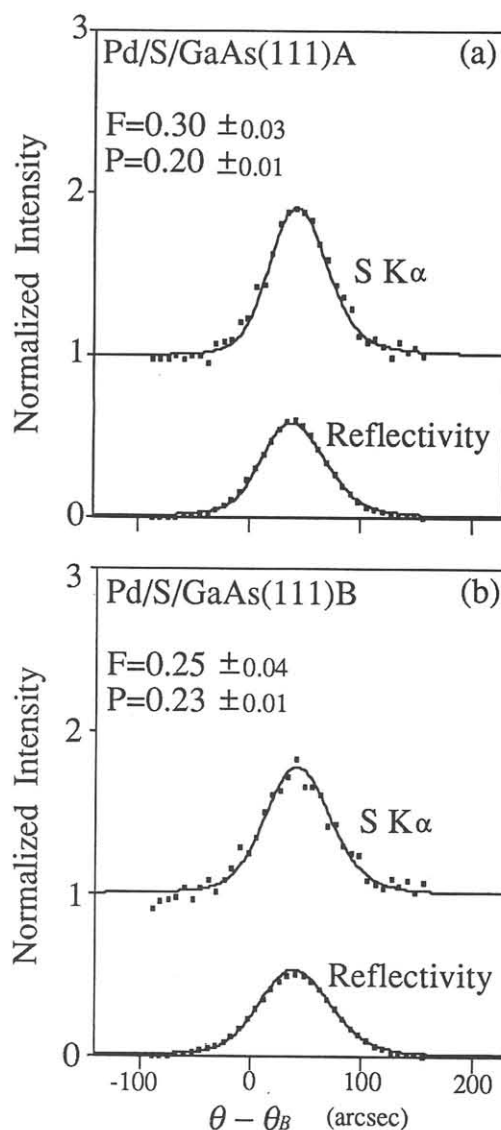


Fig.4 Angle dependence of reflectivity and S K α fluorescence yield near the (111) Bragg condition (a) for Pd/S/GaAs(111)A and (b) for Pd/S/GaAs(111)B.