

Passivation of the GaAs(100) surface with a vapor-deposited GaS film

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(Received 3 April 1998; accepted 17 July 1998)

A vapor-deposited GaS passivating layer is formed on GaAs(100) with α -Ga₂S₃ powder used as a single-source precursor for the deposition. The films grown show near-single-crystal quality, and are characterized by Auger electron spectroscopy and x-ray diffraction spectroscopy. The band-edge discontinuities of the GaS/GaAs heterojunction are determined to be 1.9 eV for the valence band and 0.3 eV for the conduction band, respectively, by ultraviolet photoelectron spectroscopy and electron-energy-loss spectroscopy. It is also observed that the valence-band structure of the GaS overlayer becomes much sharper after annealing. © 1998 American Vacuum Society. [S0734-211X(98)04205-X]

I. INTRODUCTION

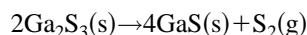
The lack of effective surface passivation of GaAs has long been a knotty problem which prohibits the development of GaAs-based devices, especially the fabrication of metal-insulator-semiconductor (MIS)-type field effect transistors (FETs). In 1987, Sandroff *et al.*¹ reported that the wet chemical treatment with inorganic sulfide solutions would lead to passivation of GaAs surfaces, which triggered a wealth of studies.²⁻¹⁰ However, the 11-ML-thick amorphous sulfide has proven to be unstable in air due to oxygen adsorption. The long term stability of the passivation effect is more likely to be accomplished with a thick sulfide layer, such as that formed by the anodic sulfurization technique.⁶ Recently, MacInnes *et al.*⁸ employed chemical vapor deposition (CVD), in which [C(CH₃)₃GaS]₄ was the precursor molecule, to form a very stable cubic phase GaS passivating film on GaAs. In our previous work,^{9,10} we reported a thick "native" sulfide formed on GaAs(100) by sulfur glow discharge (SGD). All of the investigations show that the GaS layer can indeed improve the surface properties of GaAs, e.g., a significant decrease in the surface recombination velocity is observed. Therefore, GaS is worthy of further investigations as a passivation material for GaAs from both a fundamental and practical point of view. In this article, we present a new deposition technique by vaporizing α -Ga₂S₃ and forming GaS on the GaAs surface. The Auger electron spectroscopy (AES) and x-ray diffraction spectroscopy (XRD) data reveal that a thick hexagonally crystallized GaS layer is formed on GaAs. The values of band offsets at the GaS/GaAs interface have been determined by a combined ultraviolet photoelectron spectroscopy (UPS) and electron-energy-loss spectroscopy (EELS) study.

II. EXPERIMENT

The samples used were single-crystal wafers of *n*-type Te-doped GaAs(100) with a doping concentration of

10¹⁷ cm⁻³. The surface cleaning was performed by ultrasonically washing in acetone, ethanol, and de-ionized (DI) water, in sequence, for 5 min each, followed by drying in flowing N₂. Then the wafer was dipped in a S₂Cl₂:CCl₄ = 1:2 solution at RT for 20 s to remove the native oxide and to form a S-terminated surface. After another short rinse in CCl₄, acetone, ethanol, and DI water, the sample was promptly introduced into the molecular beam epitaxy (MBE) chamber.

The sulfide layer was grown by evaporation of α -Ga₂S₃ powder from a Knudsen cell source. Prior to growth, the substrate was cleaned by heating to 500 °C for 20 min to obtain a Ga-S bond-passivated surface. The sample was kept at 200 °C during the deposition. Growth rates were monitored by a quartz microbalance at room temperature. Mass spectrometry was used to study the sulfide compounds that result from α -Ga₂S₃ vaporization. It was confirmed that in vacuum at about 720 °C, α -Ga₂S₃ loses sulfur by the reaction



and stoichiometric GaS is then formed on the substrate. Two kinds of GaS films were prepared in the present experiment. A thick (~400 nm) GaS film, used in the *ex situ* XRD and AES measurements, was grown in a separate chamber operating at a base pressure of 10⁻⁴ Pa. *In situ* UPS and EELS measurements were carried out in a VG ADES-400 angle-resolved electron spectrometer with a base pressure of 10⁻⁸ Pa, using a thin (<10 nm) film grown in an attached MBE chamber operating at a base pressure of 10⁻⁶ Pa.

III. RESULTS AND DISCUSSION

The composition and structure of the thick sulfide layer was characterized by AES and XRD. Auger electron spectra of the adlayer surface, the bulk of the layer, and the sulfide/substrate interface are shown in Figs. 1(a), 1(b), and 1(c), respectively. The primary electron energy is 3 keV. It is seen in Fig. 1(b) that the bulk of the layer only contains Ga and S.

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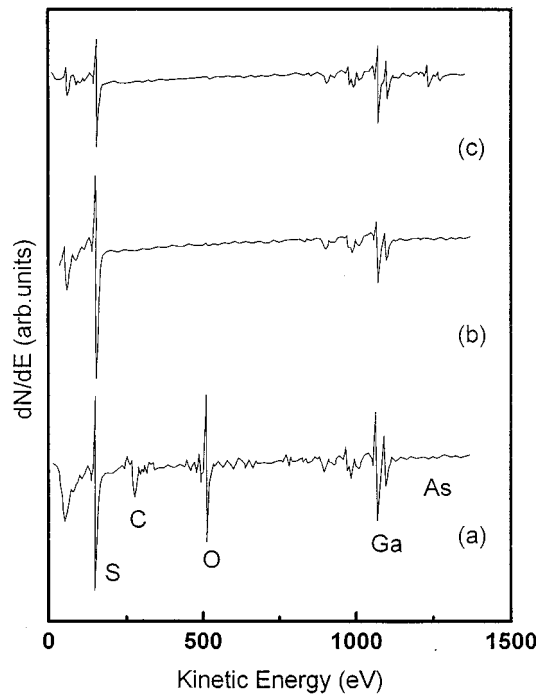


FIG. 1. AES spectra for (a) the GaS adlayer surface, (b) the bulk of GaS layer, and (c) the GaS/GaAs interface.

The O *KLL* signal is below the detection limit of AES. The depth profile shows that the compositions in the layer are fairly homogeneous and that the atomic ratio of Ga to S equals 1:1 using the known sensitivity factors whose validity was verified by Rutherford backscattering measurements. In addition, it is confirmed that the GaS/GaAs interface is clean and abrupt.

As shown in Fig. 2, XRD reveals the crystalline structure of the sulfide layer. The x-ray source is not monochromatic, so doublets appear in the spectra due to coexistence of both Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ lines. Besides the major peaks from GaAs(200), GaAs(400), and GaAs(600), two prominent diffraction peaks originating from the overlayer were recorded. According to the powder diffraction file, they can be attributed to the (002) and (004) reflections of the hexagonal crystalline phase β -GaS with lattice constants of $a=b=0.3587$ nm, and $c=1.5492$ nm. These results coincide

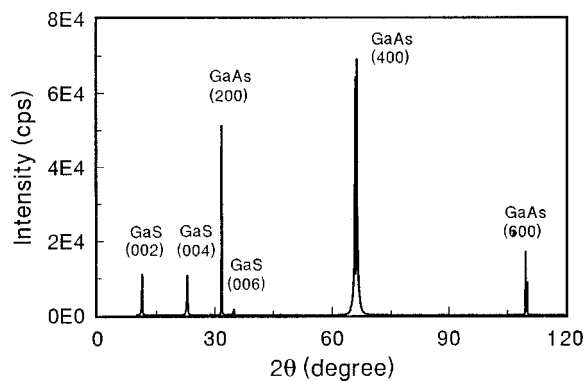


FIG. 2. XRD spectra of the GaS layer grown on GaAs(100).

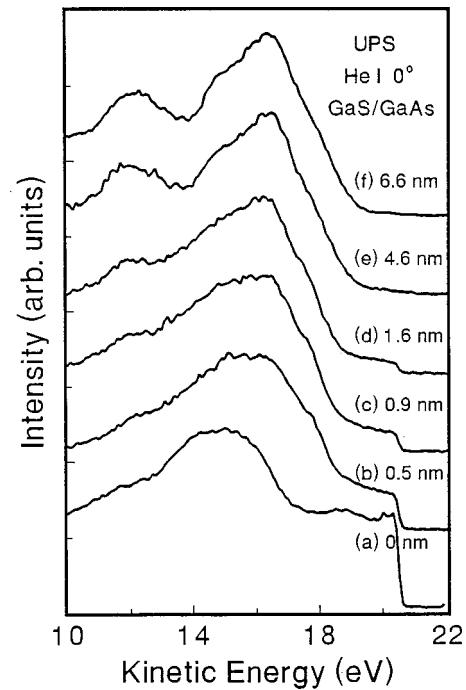


FIG. 3. UPS for the GaS overlayers of various thicknesses on GaAs(100).

well with those of SGD.¹⁰ It becomes obvious that the deposition of GaS by our method results in near-single-crystal growth, and that the growth direction is parallel to the c axis. The β -GaS crystal is constructed of identical layers. Each layer consists of four sheets of hexagonal close-packed atoms in such a manner that the Ga–Ga bonds are sandwiched by sheets of sulfur atoms.¹¹ There are four possible stacking arrangements of the complex layers leading to four polytypes designated as β , ϵ , γ , and δ . The hexagonal β phase is the most common one.

Although the β -GaS/GaAs system has a quite large lattice mismatch, there is a strong tendency of GaS to crystallize and grow along the c axis of β -GaS. For a thin film with the thickness of 40 nm, diffracted beams from many planes of GaS emerged in the x-ray diffraction pattern. When the GaS film thickness exceeded by about 80 nm, the diffraction from the (002) and (004) planes perpendicular to the c axis was dominant in the diffraction pattern. This indicates that the c axis is preferentially oriented perpendicular to the substrate during the deposition of GaS on GaAs(100). After annealing at 500 °C for 6 min, the diffraction intensities from the (002) and (004) planes increased by a factor of 2 as compared with the as-deposited sample.

Although the band discontinuities at the GaS/GaAs interface are among the most important heterojunction parameters in the fabrications of GaAs devices, to the best of our knowledge no experimental results have been reported so far. A series of ultraviolet photoelectron (UP) spectra following the deposition of various thicknesses of GaS on GaAs are shown in Fig. 3. With increasing thickness, the emission from the GaAs valence band is rapidly attenuated. The top spectrum shows the energy distribution curve (EDC) from a thick GaS overlayer, where the valence-band features of GaS dominate.

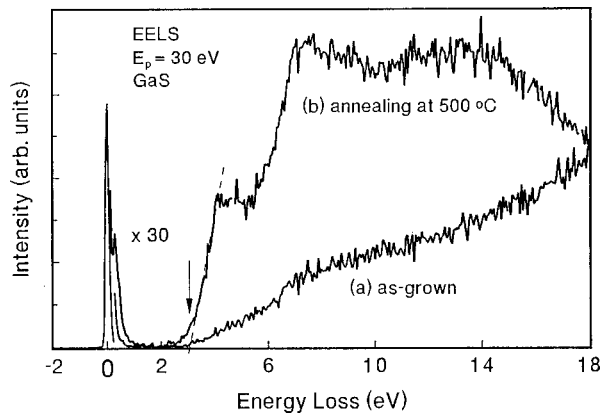


FIG. 4. EELS of the GaS layer (a) as grown and (b) upon annealing on GaAs(100).

In the curves (b), (c), and (d) with average GaS thicknesses of 0.5, 0.9, and 1.6 nm, respectively, the valence-band edges from both GaS and GaAs can be easily distinguished, so that the valence band offset of the GaS/GaAs heterojunction can be determined to be 1.9 eV. Comparing the top and bottom spectra, there is an energy difference of 1.5 eV in the valence-band edge, implying that a band bending of 0.4 eV occurs with increasing GaS thickness.

Figure 4 shows EELS spectra for a GaS film, (a) as-grown and (b) after annealing at 500 °C for 20 min. Though the electron-energy-loss structures are different, the threshold energies corresponding to the interband transition determined from curves (a) and (b) are the same, i.e., 3.0 eV. This is in good agreement with a theoretical calculation¹² which reveals a strong absorption associated with a direct gap (at Γ).

By combining the results obtained from EELS and ultraviolet photoelectron spectroscopy (UPS), a picture of band lineup of the GaS/GaAs heterojunction, as shown in Fig. 5, can be derived. The discontinuities of the valence-band edge and the conduction-band edge are 1.9 and 0.3 eV, respectively. It is worth noting that the values of the band gap at Γ point are used here in determining the conduction-band offset. Furthermore, it seems that the grown layer is weakly *n* doped as expected for not intentionally S-doped GaS crystal.

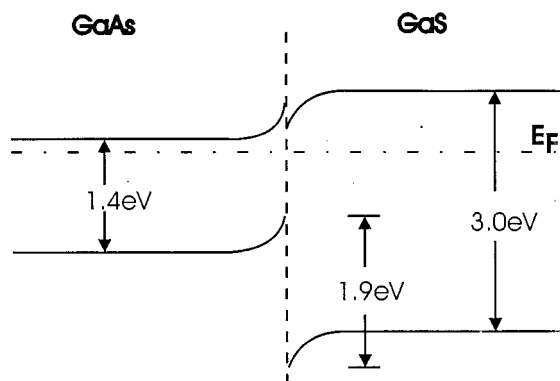


FIG. 5. Band lineup of the GaS/GaAs heterojunction.

In addition, the effect of annealing on the valence-band structure of the GaS overlayer is studied. The energy of the band edge does not change after annealing at 500 °C for 20 min. Five major peaks in the density of states plot are clearly observed within the region $E_{vb} - 10$ eV, which is fairly consistent with previous theoretical¹² and experimental^{13,14} results for GaS bulk material prepared by the Bridgeman technique.

Effectiveness of the GaS as a passivating layer has been already verified both theoretically and experimentally. Ohno and Shiraishi¹⁵ investigated the structural and electronic properties of Ga- and As-terminated GaAs(001) surfaces absorbed with 1 ML of sulfur by using the *ab initio* pseudopotential method. They found that the surface density within the GaAs energy band gap is markedly reduced by the S adsorption on the Ga-terminated surface, while no reduction of surface states was found at the As-terminated surface because the existence of band gap states originated from As-S antibonding state. The electronic properties of the GaS have also been studied experimentally in the previous work.^{16,17} Jenkins *et al.*¹⁶ fabricated a GaAs-based metal-insulator-semiconductor field effect transistor (MISFET) in which cubic GaS was used as the insulator material. Such GaS/MISFET showed an on-to-off resistance ratio comparable to that of commercial devices. Barron *et al.*^{8,16,17} have also shown that the lower interface trap densities of $\sim 10^{11}$ eV⁻¹ cm⁻² on both *n*- and *p*-type GaAs and a dramatic enhancement in the photoluminescence intensity of GaS passivated GaAs are also achieved. The similar results on the electronic properties of the hexagonal polycrystalline GaS grown on the GaAs have also obtained. The interface trap densities were reduced to be lower than 10^{12} eV⁻¹ cm⁻² and the photoluminescence from GaAs increased about two orders of magnitude.¹⁸ All of these indicate that either cubic GaS or hexagonal GaS is one of best candidate to passivate GaAs, so the understanding of GaS/GaAs interface properties is necessary to the device application of GaS as a passivating layer.

IV. CONCLUSION

In summary, by using vapor deposition, a crystalline sulfide can be grown on GaAs(100) as a stable passivating layer. The x-ray diffraction pattern of a 400-nm-thick film grown at 200 °C indicates that GaS possesses a hexagonal β -phase structure. The valence- and conduction-band offsets of the GaS/GaAs heterojunction are obtained from UPS and EELS measurements. Photoelectron energy distribution curves for the GaS film upon annealing show a sharp structure in the valence-band region. Compared with the metalorganic chemical vapor deposition (MOCVD) method of MacInnes *et al.*, this deposition technique is more compatible with existing semiconductor technology, which could permanently passivate the GaAs surface by using a simple facility and a conventional precursor. A more detailed characterization of GaS as a passivating material and its use in device fabrication is in progress.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China, Grant No. 19525410.

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