Characterization of GaS-deposited GaAs surface by XPS and PL

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Abstract   The passivation effects of GaAs surfaces by sulfur are introduced The thermal evaporation of a GaS single crystal has been used to passivate the GaAs surface The passivation effect of GaAs surface by GaS has been studied by X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) The XPS spectra show that Ga-S bonds are found to be more stable than As-S bonds These Ga-S bonds are responsible for the ... n of GaAs surfaces. PL measurements suggest that the GaAs surface is effectively passivated by a GaS films Staggered type of band alignment has been observed at the GaS/GaAs interface

1. Introduction

III V semiconductors (such as, gallium arsenide (GaAs)) have numbers of fundamental advantages over the king of semiconductors, silicon. Its application ranges from wireless communication to opto-electronics, high-speed devices and microwave-power devices. Despite intense and often disappointing efforts in the past three decades, a prominent obstacle in realizing the great potential of III-V semiconductors remains: it is difficult to grow an effective passivating and/or insulating layer with high interface quality.

The presence of high density of surface states accompanied by a large surface recombination velocity on the GaAs surfaces, leads to severe deterioration of its electronic quality. This has been considered to be a major constraint in the development of GaAs-based technology. Again, it is known that semiconductor surfaces are usually covered with native oxide layers in air. Some problem undesirable for the device fabrication process, arises from the existence of the oxide layer. Formation of surface or interface states and pinning of Fermi level are in particular, serious problems on GaAs.

In order to avoid the formation of native oxide, the surface passivation by other species of atoms is desirable for the

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improvement of their electronic quality and device fabrication. According to the definition given by Green and Spicer [1], a surface passivation layer must provide: (a) chemical passivation *i.e.*, it must prevent reactions between ambient atmosphere or other overlayers and III-V semiconductor surfaces; (b) electrical passivation *i.e.*, it must eliminate and prevent the formation of interface states; (c) an energy barrier for charge carriers at the interface *i.e.*, it must possess a sufficient barrier such that electrons will not be lost from the III-V semiconductor to the passivating layer. Sulfur and selenium are known to be useful elements for the passivation of GaAs surfaces. A lot of methods for the passivation of GaAs surfaces have been reported.

Sandroff *et al* [2] have reported for the first time that the adsorption of sulfur resulting from a wet chemical treatment in an aqueous solution of $Na_2S.9H_2O$ can lead to effective passivation of the GaAs(001) surface. A number of sources of sulfur have been shown to generate passivating layers on GaAs surfaces, whose passivation effect was lost after the sample was exposed to air for a period of time [2-8]. Recently, MacInnes *et al* [9] reported that an air-stable GaS thin film, grown by metal organic chemical vapor deposition (MOCVD) of cubic phase GaS on GaAs from a single source precursor, enhanced the photoluminescence intensity of GaAs by two orders of magnitude, which is an indication of its excellent passivation

effect. Hou and coworkers have reported that sulfur passivations by the electrochemical technique of $(NH_4)_2S$ [10, 11] and by glow discharge of sulfur [12] are very stable and long lived passivation techniques.

We have used the layered-semiconductor GaS for the passivation of GaAs surface [13-16]. The single crystal GaS was thermally deposited on GaAs substrates. The initial stage of the growth of GaS thin films on GaAs(111)A and (001) surfaces has been investigated *in-situ* by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low-energy electron-loss spectroscopy (LEELS) and *ex-situ* by PL. In these studies, we have reported that GaAs surface was effectively passivated by GaS thin films.

In this article, we report the bonding states of S-atoms and GaAs surfaces studied by XPS. Passivation of the GaAs surface by GaS thin layers as verified by the low temperature PL spectrum has also been reported. An energy band diagram has been proposed between GaS and GaAs interface.

2. Experimental details

GaS films were grown and all measurements (except PL) were carried out in an ultrahigh vacuum chamber (ULVAC PHI 548-SH, ESCA/AES system) with a base pressure of $\sim 2 \times 10^{-9}$ Torr at Toyama University. The chamber was equipped with a double-pass cylindrical mirror type energy analyzer (CMA) for the measurement of AES, LEELS and XPS. The substrate was *n*-type GaAs(001) wafers prepared by ultrasonic cleaning in acetone, methanol solutions and de-ionized water. No chemical etching was performed before loading the substrate into the vacuum chamber. After introducing the GaAs substrate into the chamber, the surface was cleaned by Ar+ ion sputtering with an accelerated voltage of 1.0 keV, and subsequent annealing at 400°C for 30 min. After these treatments, AES showed no contaminations such as carbon and oxygen on the surface.

The sublimated materials were GaS crystalline ingots grown by the Bridgman method in our laboratory. They were heated in a coiled tungsten filament, and the evaporation rate in a series of experiments was constant, which corresponded to a growth rate of about 0.1 Å/sec on the GaAs substrate at room temperature. The thickness of GaS films was monitored by a quartz oscillator, and estimated by the AES signal intensity of As(LMM) at 1228 eV from the substrate with using the mean free path of the electrons (21.1 Å). Mg-Kα X-rays (1253.6 eV) were used as an excited source in XPS measurement. The PL measurements were carried out at 5.5 K using a Jobin Yvon HR 250 Spectrometer with the 5145 line of an Ar+ laser as an excitation source and emission signals were detected by a Ge detector cooled by liquid nitrogen. The power density on the sample surface was about 0.4 W/cm².

3. Results and discussion

3.1 Bonding states of sulfur-atoms and substrate surfaces

The XPS spectra provide useful information for understanding the chemical bonding states of the constituent atoms, and have been widely used for the study of S-passivation of GaAs surfaces.

Figure 1 shows the XPS spectra of Ga 3d (left) and As 3d (right) for GaS films grown on GaAs(001) substrates using GaS single crystal as an evaporation source. In Figure 1, (a) are spectra of GaS film grown on GaAs(001) surface at 350°C and (b) are those of GaS film annealed at 500°C for 1 hr after the growth at 350°C, (c) are those of GaS film grown on GaAs(001) surface at 400°C and (d) are those of GaS film annealed at 500°C for 1 hr after the growth at 400°C. Although the Ga 3d peaks for GaS film grown on GaAs surface seem to be a single peak, it is slightly broader than the peak for the cleaned GaAs surface, where both Ga-As bonds exist. Therefore, they were deconvoluted into two components using Gaussian line shape, where the widths were chosen from the Ga 3d spectra, approximated by Gaussian distribution, of the respective substrate. The peak with lower binding energy corresponds to the Ga-As bond in GaAs substrate. The remaining sub-peak at higher binding energy side is thought to be due to Ga-S bonds [10, 13, 14, 17, 21]. For both temperatures, the intensity of the Ga-S component relative to that of Ga-As slightly increases after annealing, albeit the film thickness decreases, as seen in Figures. 1(b)(left) and 1(d)(left). The increase of peak intensity after annealing at 500°C is probably because of the improvement in the crystal quality.
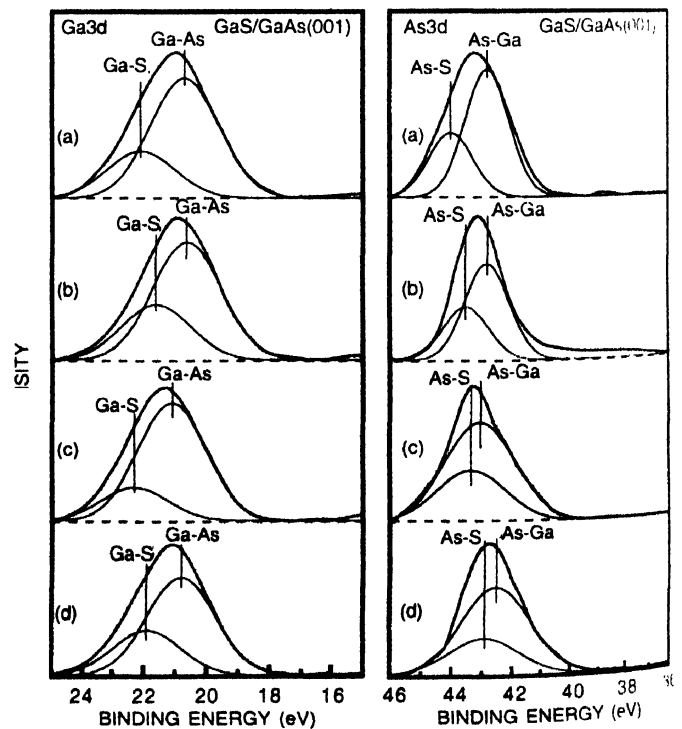

Figure 1. Ga 3d (left) and As 3d (right) XPS spectra: (a) as-deposited GaS film grown on GaAs(001) at 350°C, (b) after annealing at 500°C for 1 h of sample (a), (c) as-deposited GaS film grown at 400°C, (d) after annealing at 500°C for 1 h of sample (c)

the films. Furthermore, S atoms which were bonded to As atoms at the S-passivated GaAs surface moved to Ga atoms to form stable Ga-S bonds as a result of thermal annealing, being agreement with the evolution of As 3d XPS spectra upon annealing as discussed in the following paragraph.

Like Ga 3d spectra, As 3d peaks were also deconvoluted into two components using Gaussian line shape. For both temperatures, the lower binding energy peak is the substrate As-Ga component, which dominates after annealing at higher temperature. The higher binding energy peak is ascribed to be due to As-S bonds [10, 13, 14, 17-21]. These As-S bonds may be present at the interface between GaAs and GaS. After annealing at higher temperature, the intensity of the As-S component relative to that of As-Ga decreases, which indicates the movement of S atoms from As to Ga atoms to form thermodynamically more stable Ga-S bonds than As-S bonds.

3.2 Enhancement of photoluminescence properties by sulfur-passivation :

The enhancement of PL intensity from GaAs is often used as a measure of surface quality following surface treatment procedures. A reduction in the density of surface impurities responsible for midgap states results in reduced band bending and/or a reduction in the effective surface recombination velocity, thereby increasing the net PL efficiency (i.e., quantum yield) of the surface treated samples [22]. The passivation effectiveness can thus be checked using photoluminescence.

Several groups of researchers have reported the enhancement in PL intensity of GaAs(001) samples after (NH$_4$)$_x$S-treatment [4, 10, 11]. The PL intensity increased after the S passivation compared with that of the as-etched surface. However, in the case of ordinary S passivation in (NH$_4$)$_x$S solution, a rapid decay of PL intensity was observed under Ar$^+$ laser illumination with 5145Å line, which was explained as the photon-assisted oxidation effect. On the other hand, the PL intensity from samples treated by the anodic S passivation in (NH$_4$)$_x$S solution remained unchanged under the same illumination condition for 30 minutes. [10-12]. MacInnes *et al* [9] have deposited a very stable cubic GaS thin film on a GaAs surface by the metal organic chemical vapor deposition (MOCVD) technique [9]. They have reported that the PL peak intensity increased after treatment as compared with that before growth and there was no significant change in PL intensity even after storage in ambient laboratory conditions for a period of four months after deposition.

In our experiment, the passivation effect of GaS on GaAs surfaces was evaluated by measuring the PL peak intensity of band-to-band luminescence at around 1.51 eV of GaAs before and after the growth of GaS thin films at 400°C [15, 16]. The PL intensity was recorded at 5.5K as a function of aging time in the atmosphere, as shown in Figure 2. The shape of PL spectrum

was not changed with aging time. The magnitude of PL intensity increases after the deposition of GaS films as compared with that of clean GaAs surfaces. For GaAs covered by GaS, there is no significant change of the magnitude of PL intensity with aging time. Our result also shows that after the deposition, GaS layers act as a protector for the S-passivated GaAs surface.
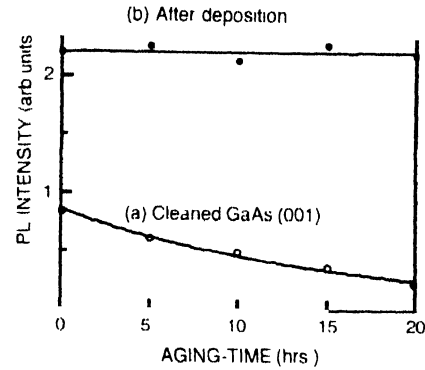

Figure 2. PL intensity of GaAs(001) at 5.5 K as a function of aging time in atmosphere (a) as-cleaned, (b) after deposition of GaS films on GaAs(001) at 400°C followed (a) by annealing at 500°C

3.3 Energy band diagram for the GaS/GaAs(001) interface :

We have studied an energy band diagram of GaS-covered GaAs using XPS measurements of the band discontinuities [14]. The interface band discontinuities are among the most important parameters characterizing the behaviour and performance of heterojunction devices. Although several theories have been proposed to estimate the band discontinuities, reliable values can only be obtained experimentally.

In the present study, the band discontinuities at the interface between GaS and GaAs(001) surface were measured by an 'indirect method of band discontinuity estimation by XPS'. In this method, the valence band discontinuity ΔE_v at the GaS/GaAs interface is estimated by measuring the XPS spectra of the valence band and core levels [23, 24]. ΔE_v is given by

$$\Delta E_v = \left(E_v^{GaS} - E_{S2p}^{GaS}\right) - \left(E_v^{GaAs} - E_{As3d}^{GaAs}\right) + \Delta E_{Cl} , \quad (1)$$

$$\Delta E_{Cl} = \left(E_{S2p}^{GaS} - E_{As3d}^{GaAs}\right) , \quad (2)$$

where E_v^{GaAs} and E_v^{GaS} are the valence band maxima (VBM) of bulk GaAs and bulk GaS, respectively, and E_{As3d}^{GaAs} and E_{S2p}^{GaS} are the core level energies of As 3d of bulk GaAs and of S 2p of bulk GaS, respectively. ΔE_{Cl} is the energy difference between As 3d and S 2p when the GaS films are deposited onto GaAs. The valence band maxima are difficult to locate with good accuracy. The valence band spectra of the ultrasonic cleaned, Ar$^+$ sputtered and heated (bulk) GaAs and ex-situ cleaved (bulk) GaS surfaces are shown in Figure 3, where the VBM positions

were determined by a linear extrapolation of the leading edge of the valence band spectra.
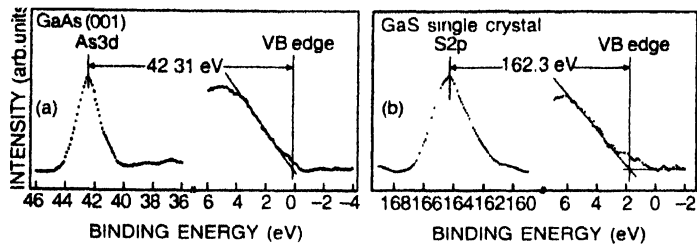

Figure 3. Core level and valence band spectra of (a) GaAs(001) surface. (b) cleaved GaS surface

The Fermi level of GaAs is estimated to be 0.46 eV above the valence band edge. The value of $\left(E_v^{GaAs} - E_{As3d}^{GaAs} \right)$ for GaAs was determined from the measurement of core level and valence band spectra of the substrate, as shown in Figure 3(a). The value was averaged for three sets of measurements, and is thus obtained as -42.31 ± 0.1 eV. Similarly, the value of $\left(E_v^{GaS} - E_{S2p}^{GaS} \right)$ for GaS was determined from the measurement of core level and valence band spectra of the GaS single crystal, as shown in Figure 3(b). It was obtained to be -162.3 ± 0.1 eV. The Fermi level of GaS is estimated to be 1.72 eV above the valence band edge. ΔE_{cl} was measured for the GaS film on GaAs(001) surface deposited at 400°C followed by an anneal at 450°C, and was estimated to be 120.13 eV. The deconvoluted peaks for As $3d$ and S $2p$ were used for the estimation of ΔE_{CL}. Substituting these results in eq.(1), the valence band discontinuity at the GaS/GaAs interface is obtained as $\Delta E_v = 0.14 \pm 0.2$ eV. The band gaps of GaAs and GaS are 1.43 and 2.5 eV, respectively. Therefore, the conduction band discontinuity (ΔE_c) at the GaS/GaAs(001) interface was calculated by using the following equation

$$\Delta E_c = \Delta E_v + \left(E_G^{GaS} - E_G^{GaAs} \right) = 1.21 \pm 0.2 \text{ eV. Using the values}$$

obtained for ΔE_v, ΔE_c and ΔE_{CL}, the energy band diagram can be drawn as in Figure 4, which is known as a staggered type of band alignment.
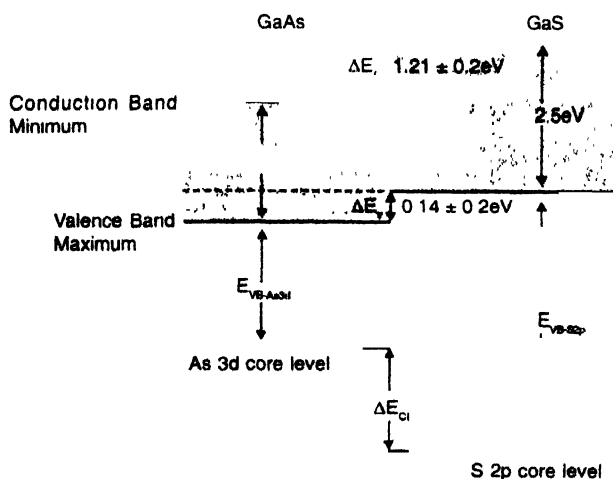

Figure 4. Schematic energy-band diagram at the GaS/GaAs(001) interface

This type of band alignment has also been reported by Takatani *et al* [25] for the growth of amorphous Se on GaS surfaces.

4. Conclusions

The passivation effects of GaAs surfaces using sulfur has been characterized. It has been shown that sulfur is an important element for the effective passivation of GaAs surfaces. Ga-bonds were found to be more stable than As-S bonds. The Ga-S bonds are responsible for the passivation of GaAs surface by reducing the surface state density within the energy gap, GaAs. Photoluminescence measurement has been used to check the effectiveness of the S-passivation. To keep the passivation effect long lived, the growth of protective layer of GaS effective. The band alignment at the GaS/GaAs(001) interface has been shown to be a staggered type, and the valence and conduction band discontinuities have been estimated to be 0.1 eV and 1.21 eV, respectively.

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