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Regular distribution of S or Se in $(NH_4)_2S_x$- or Na_2Se/NH_4OH-treated GaAs surfaces

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Passivation of surface for stabilizing it during device process is a crucial issue in the development of compound semiconductor technology and the performance of microelectronic and optoelectronic devices[1-3]. It has been announced that electronic and optical properties of GaAs surface is drastically improved by passivating the surface with sulfur using Na_2S, $(NH_4)_2S$, $(NH_4)_2S_x$, and H_2S. In particular, the $(NH_4)_2S_x$-treatment was more effective to stabilize GaAs surface than the others[2]. Passivation with Se gas flux, Na_2Se and the other solutions containing Se, has also shown to be a promising one. Se-passivated GaAs has been reported dramatic photoluminescence gain and stability against photo-oxidation than the sulfide compartments[3]. However, this ultra-thin passivation layer is difficult to control and characterize effectively, hence there are many discrepant results.

In this study, we report the atomic distribution of HCl-etched and S or Se-passivated GaAs surface. ARXPS was employed to investigate the qualitative and quantitative distribution of bonding states in near surface layers. The resultant atomic distribution of etched and passivated GaAs surface was correlated with the results of LEED.

All the surface treatments of cleaning and passivation processes were done on undoped GaAs (100) substrates within an atmospheric controlled glove box with nitrogen. The samples were first degreased by immersing in boiling acetone for 10 min, in methanol for 5 min, and in deionized water (DIW) for 1 min successively. Native oxide on GaAs surface was then removed by the treatment with concentric HCl for 3 min and DIW-rinse for 1 min. HCl-treated GaAs surface was also treated with $(NH_4)_2S_x$ or Na_2Se/NH_4OH solutions for 10 min and followed by DIW for 1 min. $(NH_4)_2S_x$ ($x \fallingdotseq 2.3$) solution was prepared by adding excess S powder (Aldrich, 99.999 %) in $(NH_4)_2S$ solution and Na_2Se/NH_4OH solution was prepared by mixing 1M Na_2Se solution with NH_4OH solution to the ratio of 1 : 2. For XPS measurements, the excitation was accomplished using monochromatized Al kα radiation source in VG Scientific ESCALAB220i-XL. Narrow scan spectra of all regions of interest were recorded with 20 eV pass energy. Take-off angle between sample surface and detector was varied from 20 to 90 with a step of 5. LEED was employed to observe 2-dimensional surface structure of HCl-, $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treated GaAs with variation of incident electron beam energy.

Fig. 1 corresponds to (a) Ga 3d and (b) As 3d core level spectra obtained at 30° of take-off angle after HCl-, $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treatments, respectively.

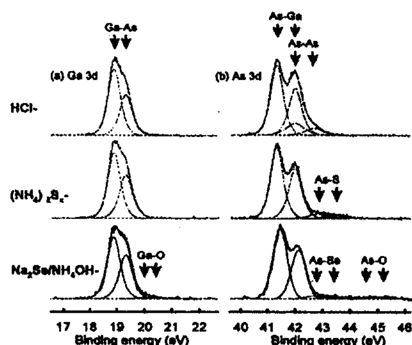

Fig. 1. XP spectra (a) Ga 3d and (b) As 3d from GaAs surfaces just after HCl-, $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treatments, respectively.

Both Ga 3d and As 3d spectra exhibit two orbital energy level as $3d_{5/2}$ and $3d_{3/2}$ (spin-orbital coupling) with 0.45 and 0.70 eV of splitting, respectively. All samples show Ga-As bonding at center of 19.0 eV in Ga 3d spectrum and 41.3 eV in As 3d spectrum. Another is observed As-As bonding (elemental As) at center of 42.0 eV in HCl-treated GaAs. $(NH_4)_2S_x$-treated GaAs includes As-S bonding at 43.9 eV together with As-Ga bonding, however any elemental As is not observed. In Na_2Se/NH_4OH -treatment, As-Se bond of 42.8 eV and As-O bond of 44.2 eV in As 3d spectrum and 20.3 eV of Ga-O bond in Ga 3d spectrum are also observed. In the HCl-treated sample, the occurrence of elemental As results from the preferential etching of Ga, as reported in the previous study[4]. In the As 3d

spectrum as shown in $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treated GaAs surfaces of Fig. 1, the disappearance of elemental As and the generation of As-S or As-Se bond indicate the transition of As-As bond to As-S of As-Se bonds during the S or Se passivation. The presence of Ga and As oxides was seemed to be due to the OH^- contained in the passivating solution.

Fig. 2(a), (b), and (c) show the angle dependency of absolute counts of surface constituents after HCl-, $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treatments, respectively.

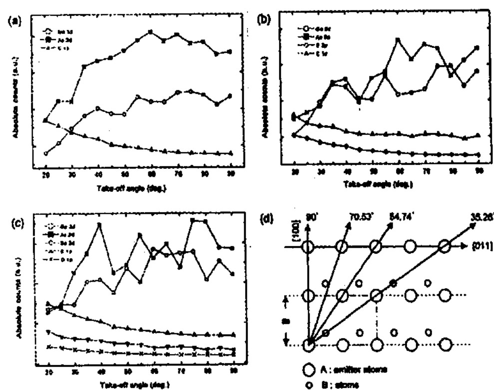

Fig. 2. Angle dependency of photoelectron intensities; (a) HCl-, (b) $(NH_4)_2S_x$-, (c) Na_2Se/NH_4OH-treated GaAs surfaces, and (d) cross-sectional distribution of (100) plane in zincblende structure, respectively.

Photoelectron intensities of C, S or Se decrease with take-off angle, while those of Ga and As increase. In Fig. 2(a), (b), and (c), As/Ga ratio of HCl-treated GaAs is higher than that of $(NH_4)_2S_x$- or Na_2Se/NH_4OH- treated one. This is from the larger amount of As-As bonds than that of As-S or As-Se bonds, as shown in Fig. 1(b). This means that all of the elemental As does not react with passivating species (S or Se) and form the passivation layer. And some of elemental As is etched during the passivating treatment. In particular, Ga and As species clearly exhibit oscillation of photoelectron intensity compared with C and S or Se. This phenomena is seemed to be due to diffraction effect, strong intensity enhancement in angular photoelectron intensity distribution along the internuclear axis which connects the emitting atom with its nearest and next-nearest neighboring atoms, as shown Fig. 2(d). Hereby, the oscillation in $(NH_4)_2S_x$- and Na_2Se/NH_4OH-treated GaAs was more rugged than in HCl-treated one. It can be thought that the S or Se is arrayed more regularly than elemental As. Fig. 3(a), (b), and (c) show the LEED patterns of various GaAs surfaces, respectively.

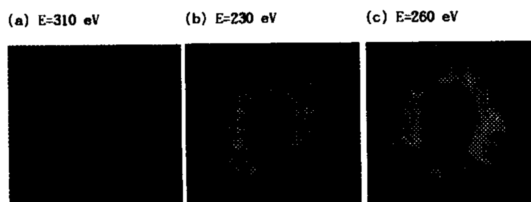

Fig. 3. LEED patterns ; (a) HCl-, (b) $(NH_4)_2S_x$-, and (c) Na_2Se/NH_4OH-treated GaAs surfaces, respectively.

Whereas the HCl-treated GaAs surface failed to give a LEED spot pattern, several weak diffraction spots were observed after $(NH_4)_2S_x$- or Na_2Se/NH_4OH -treatments. These patterns were observed in the energy region of 200~400 eV, where the inelastic mean free path is about 10Å (about 2~3 monolayers). This indicates that elemental As was randomly distributed on GaAs surface, while As and S (or Se) atoms which form As-S (or Se) bonding, were regularly distributed. And this result confirms different intensity oscillations in HCl-, $(NH_4)_2S_x$-, and Na_2Se/NH_4OH-treated GaAs, as shown in Fig. 2.

In $(NH_4)_2S_x$- and Na_2Se/NH_4OH-treated GaAs, the disappearance of elemental As and the generation of As-S or As-Se bonds were observed. And the more rugged oscillation of photoelectron intensity of Ga and As was observed than the HCl-treated one. Through the analyses using LEED, the elemental As after the HCl-treatment was revealed to be randomly distributed on the GaAs surface, and the passivating species S or Se, were regularly distributed on GaAs surface just after S or Se-passivation treatments.

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