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Surface Chemical Bonding of Selenium Treated GaAs(100)

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The passivation of GaAs(100) by Se prepared in-situ has been studied in detail by Synchrotron Radiation Photoelectron Spectroscopy(SRPES). Deposition of Se on GaAs with the substrate held at room temperature yields As-Se bonding with little band bending reduction. Few changes are observed both in band bending and chemical bonding as the sample is heated to 250°C. In contrast, deposition of Se on GaAs at a substrate temperature of around 580°C gives rise to Ga-Se bonding as Se exchanges with As not only at the surface layer but penetrates into bulk layers as well.

1. Introduction:

Recently, Se has shown promise as a new passivation material for GaAs[1-3]. The advantages in using Se over S include MBE compatiability and a radius that is closer in size to both As and Ga. While the effects of Se passivation are now being explored, very little work to now has been focused on understanding the mechanism of GaAs passivation by Se and on how it differs from S passivation.

In this paper, we report on the surface chemical bonding of Se to GaAs and how this is related to the temperature of the GaAs substrate during Se deposition. By doing this we can explain to a large extent the basic nature of GaAs passivation by Se.

2. Experimental:

The samples were n type GaAs wafers(Si doped) with a carrier density of $1x10^{18}$ cm^{-3}. The GaAs wafers were first rinsed in acetone and then purified water before dipping in a commercial alkaline based etchant for 5 minutes. Following this, the sample was rinsed in purified water and dried with N_2(g). The etched GaAs wafers were then attached to a Mo sample holder with In solder and placed in a vacuum chamber connected to both an analysis and MBE chamber.

Following this, the sample was heated in an As overpressure for about 5 minutes at 600°C to desorb the surface oxides. The temperature was then lowered to about 550°C where a GaAs epitaxial layer was grown with a As_4/Ga flux ratio of about 10 and a fine streaky 2x4 RHEED pattern was observed. The substrate temperature was then lowered and the structure changed from 2x4 to 2x1. The sample was then transferred to a combined surface analysis system[4] which is located at the Photon Factory on beam line BL-1A in Tsukuba. Synchrotron Radiation Photoemission Spectroscopy (SRPES) and XPS(Al Kα) measurements were then performed on the samples. Following this, the sample was returned to the MBE chamber where Se deposition was performed either at room temperature(RT) or at elevated temperatures near 580°C. The temperature of the substrate in all cases was measured directly by an optical pyrometer. In the Se deposition, the Se flux was 3.6×10^{-6} torr at 130°C(room temp. Se dep.) and 2.2×10^{-5} torr at 150°C(high temp. Se dep.). A schematic of the instrument and the experimental procedure is shown in figure 1.

The synchrotron photon energy was adjusted to 90.0 eV using a grating/crystal monochromator[5]. The incident photon energy calibration and energy resolution evaluation(0.3 eV) was made by directly measuring the Fermi edge of Au.

3. Results and Discussion:

The analysis begins with the As rich clean GaAs surface. In fig. 2, the As 3d spectra are plotted for the various surface treatments. One can observe that the As 3d peak in fig. 2 corresponding to the As rich clean 2x1 surface is fit nicely with two peaks separated by 0.4 eV where the higher binding energy peak is assigned as surface As.

The next case corresponds to the case where GaAs was exposed at RT to a Se beam for 5 seconds. Drastic changes are observed in the As

3d spectra for this treatment. In particular, a high binding energy peak of large intensity is observed. Based on the Ga, As and Se electronegativity values of 1.82, 2.20 and 2.48 respectively[6], one can assign the high B.E. peak as originating from a As-Se peak with a slight formal positive charge localized on the As atom since Se is the more electronegative element. There is very little change in the Ga 3d spectra between the clean GaAs surface and the Se treated GaAs surface indicating that there is no interaction between Ga and Se at this stage, as discussed in greater detail in another report[7] The next step involved heating the GaAs substrate to 250°C for 10 minutes in vacuum. In the case of GaAs treated with (NH4)2Sx, S was observed to replace As, bond with Ga and reduce band bending at an annealing temperature of approximately 200°C[8,9]. In fig. 2, one can see that the Ga-As peak grows in relative intensity and the As-Se peak decreases by about half of its original intensity indicating that about half of the surface As is desorbed during annealing. The peak binding energy of the As 3d Ga-As component indicates very little band flattening at this annealing temperature suggesting that the GaAs surface is not passivated at this point. These results also suggest that the chemistry of Se and S passivation is quite different. As mentioned above, conversion of As-S to Ga-S takes places with nearly 100% conversion at temperatures well below 250°C suggesting the activation energy barrier for this conversion is considerably lower than the As-Se to Ga-Se conversion. This is nonetheless not very surprising based on the greater ionicity and the greater heat of formation of Ga-S relative to Ga-Se[6,10].

The next step involved a new GaAs sample and preparing the sample in the MBE chamber in a manner similar to that described before. The Ga 3d, As 3d and valence band spectra were virtually identical for the As rich clean GaAs surfaces for the two different samples insuring that the surfaces and starting conditions were also virtually identical. Following this, the sample was heated in an As_4 overpressure at 580°C. During this time, the As beam shutter was shut and the sample was exposed to the Se flux for 5 minutes. Following this, the sample was cooled and continuously exposed to a Se flux until the sample temperature reached 400°C at which time the Se shutter was closed and the sample was transferred to the analysis chamber. A 2x1 RHEED pattern was observed prior to Se treatment and was maintained with Se treatment.

The As 3d spectrum shown in fig. 2 for the high T Se deposition is rather simple and is fit with only one peak clearly indicating that any last vestiges of As-Se bonding have disappeared. In addition, the As 3d spectrum as a whole shifts to higher binding energy, especially with respect to the As-Ga component of the previous 250°C anneal As 3d spectra, indicating a reduction in band bending.

Finally, the sample was heated in the analysis chamber in vacuum until the Se was desorbed, which for the GaAs(100) crystal face was about 630°C. The Ga rich (100) spectra show a large number of defect states, a spotty RHEED

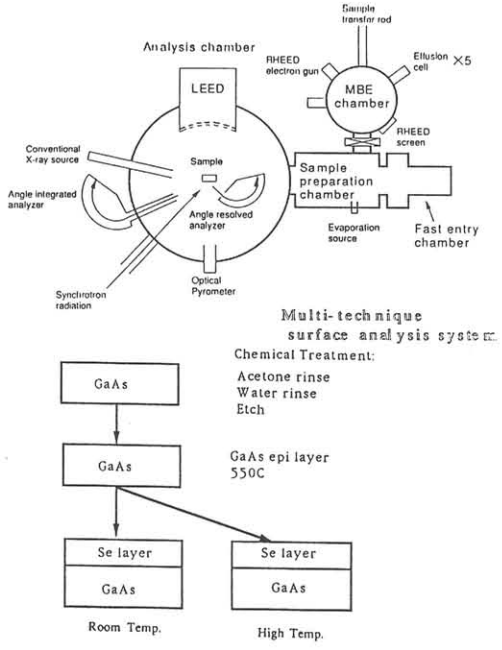

Fig. 1 The top half of this figure is a schematic of the instrument used. The bottom half describes the experimental procedure.

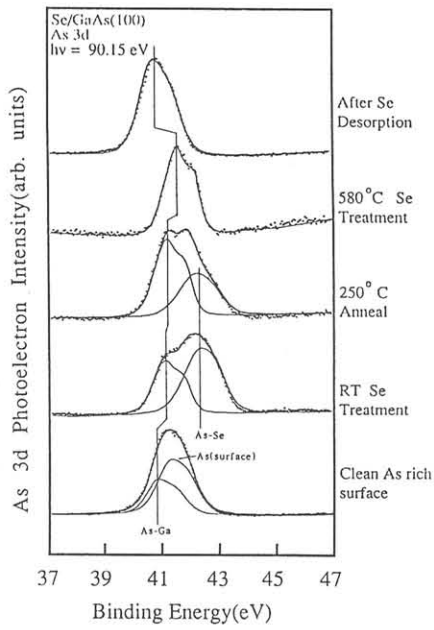

Fig. 2 The As 3d spectra are plotted under the conditions written on the right.

pattern as well as an increased in band bending as well, as can be seen in the As 3d spectrum plotted in fig. 2.

The Se 3d spectum for the 550°C Se deposition is shown in fig. 3. The large spin orbit splitting of 0.83 eV gives the final spectra a shape where three large peaks are observed. The $3d_{5/2}$ component of the lower B.E. Se peak nearly coincides with the $3d_{3/2}$ component of the higher B.E. Se peak. The higher B.E. Se is assigned to surface Se. The lower B.E. Se is attributed to Se in the third and possibly fifth layer of GaAs substituting with As. In this case, one would expect a lower B.E. for Se incorporated below the GaAs surface layer since one would expect more complete charge transfer from Ga to Se since Se is coordinated to four Ga atoms. In contrast, surface Se for the (100) case is only coordinated to two Ga atoms hence one would expect a higher binding energy since there is less charge transfer from Ga to Se.

The picture that emerges can be visualized more easily in fig. 4 which is a side view of the Se passivated GaAs(100) surface. The first surface layer is terminated with Se atoms with no dangling bonds since Se is a group VI atom. The third layer has a fraction x of Se atoms substituting for As atoms and a fraction (1-x) of As atoms that remain. One may expect this fraction to depend on conditions such as substrate temperature, Se pressure etc. Based on the relative peak areas of the surface and bulk Se 3d peaks, a value of 0.90 was obtained for the Se incorporation in the third layer.

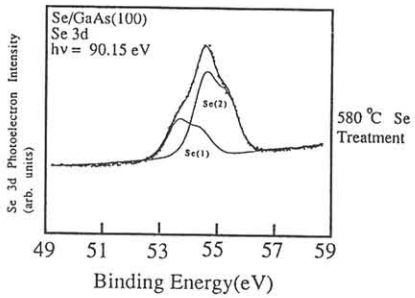

Fig 3 The Se 3d spectrum is plotted for the high temperature deposition.

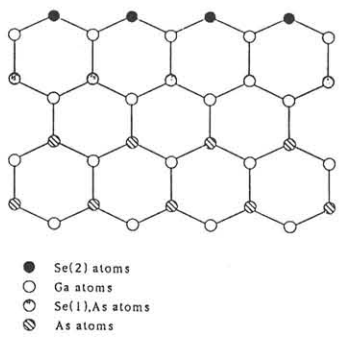

Fig 4 Proposed model for Se/GaAs(100) for the high temperature Se deposition case.

Finally we are in a position to make a quick comparison of the surface passivation of GaAs by either S or Se. The results are succinctly tabulated in table 1 below.

	S	Se
Coverage	1ML	2ML
Band Bending Relaxation	0.4eV	0.2eV
Effectiveness	Fair	Good

Table 1: Comparison of Se and S passivation of GaAs

The results indicate that Se is overall slightly more effective at passivating the GaAs surface than S. Nevertheless, much work remains to be done, in particular concerning the relative stability of the Se or S layer upon overlayer deposition.

4. Conclusion:

The passivation of GaAs by Se in vacuum has been clarified by surface sensitive SRPES. The results indicate that passivation of GaAs does not occur when the substrate is held at RT during Se deposition. Furthermore, the activation barrier for As-Se to Ga-Se is slightly higher than the As-S to Ga-S barrier. It is found that even at 250°C, surface As persists even if it is bonded to Se and that band bending is not significantly reduced. In contrast, if depostion is made at a relatively high substrate temperature, surface As is completely substituted by Se and a certain amount of As to Se substitution occurs in the bulk layers as well. With Se bonding exclusively to Ga and the disappearance of surface As, band bending is reduced(but not eliminated) considerably to about 0.2eV.

5. References:

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