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Surface passivation of III-V compound semiconductors with chalcogen atoms

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Keywords: Surface passivation, chalcogen treatment, III-V compound semiconductor, interface state density, surface analysis

Abstract

Surface passivation of III-V compound semiconductors with chalcogen atoms (S, Se, Te) is presented in the light of electrical characteristics and data on surface analyses. The chalcogen treatment is effective for the reduction in surface/interface defect density and the effect is universal to many III-V compounds. Based on the experimental data, we propose a model to explain its effectiveness, and suggest the surface stabilization by chalcogen. Structurally, chalcogen atoms occupy the near-site of V elements on top of the surface and III-chalcogen bonds are formed. Such a structure may be stabilized through charge transfer of excess electrons into the dangling bond states.

Introduction

The apparent success of Si in electronic devices and integrated circuits depends essentially on controlling its surface/interface properties. However, those of III-V compound semiconductors remain uncontrollable to date, except for the use of heterojunctions, initially, of GaAs/AlGaAs. In particular, the presence of oxygen at the surface induces an increase in the surface recombination velocity (SRV), and degrades the performance and reliability of surface devices. In recent years, several surface treatments with sulfide solution were developed to suppress the SRV, in other words, to increase the photoluminescence (PL) intensity. The first of such is sodium sulfide ($Na_2S \cdot 9H_2O$) treatment on GaAs reported by Sandroff *et al.*[1] Although it is recognized that Na_2S treatment produces a decrease in SRV, it is difficult to tell whether the effect is due to the reduction in the surface state density or in the capture cross section of defects caused by band bending. This is because the residual crusty film of Na_2S prevents us from fabricating the devices to measure its electronic properties. Moreover, the effect is easily lost after rinsing its film in water, and an accumulation of Na^+ ions on the surface is undesirable for the MIS devices.[2]

So we tried other chemicals and found more effective and dependable surface treatments on GaAs with ammonium sulfide ($(NH_4)_2S$) and ammonium polysulfide ($(NH_4)_2S_x$) solutions with excess sulfur. In order to clarify the difference in treatment effect of $(NH_4)_2S/(NH_4)_2S_x$ from Na_2S, we investigated the surface in both aspects of electrical characteristics and structures. We also compared the effect on various III-V compounds of GaP, (AlGa)As, InP and InAs with that on GaAs, because it is expected that the process is applicable to heterostructure devices. Electrical characteristics of Schottky and MIS structures were measured to estimate the density of surface/interface states. Surface structure was examined by using various surface analysis techniques such as Auger electron spectroscopy (AES), low-energy electron energy loss spectroscopy (LEELS), photoemission spectroscopy (PES) and reflection high-energy electron diffraction (RHEED). Based on those experimental data, we propose a model to explain the universal effectiveness of $(NH_4)_2S_x$ treatment on III-V compounds. Our model is extended to the surface treatment with chalcogen atoms other than S, that is, Se and Te. The exact position of chalcogen adsorbates in respect to the host atoms of substrate was determined by means of coaxial impact collision ion scattering spectroscopy (CAICISS), scanning tunneling microscopy (STM) and X-ray standing wave (XSW) techniques. Finally, we examined the oxidation of chalcogen-passivated surface, because the effect slowly and mildly degrades in room air.

$(NH_4)_2S_x$ treatment on III-V compound semiconductors

The procedure of $(NH_4)_2S_x$ treatment follows a simple wet process. A sample etched in a normal way is dipped into the treatment solution. We used the $(NH_4)_2S_x$ solution with 8 % of sulfur, which is readily available from venders. After taking off the sample out of solution, droplets on the surface are blown off with a dust-free jet of N_2. In this stage, a thin yellowish film of amorphous sulfur is usually observed. In vacuum at room temperature (RT), however, the surface changes its appearance from yellowish to shiny crystalline reflection because of a sublimation of amorphous sulfur. As described later more in detail, the treated surface is stabilized by heating between c. 250 °C and 520 °C in vacuum. The heat treatment is essential in obtaining a stabilized surface.

Figure 1 shows the difference in Schottky barrier height (SBH) on III-V compound semiconductors between before and after the treatment. In Fig. 1(a), it is clear that SBHs on the as-etched surfaces of GaP, GaAs and InP are almost unchanged, whereas those on the treated surfaces vary with the work function of deposited metal. According to a simple interfacial layer model, it is suggested that SBH on the treated surface approaches to the calculated value assuming no pinning traps. In other words, the $(NH_4)_2S_x$ treatment is effective for a decrease in the interface state density. This holds true also in (AlGa)As with the different contents of Al, as shown in Fig. 1(b). The similarity of these electrical properties assures the effectiveness of the $(NH_4)_2S_x$ treatment on III-V compounds, though the quantitative difference suggests the difference in effectiveness of the treatment.[3]

The reduction in the interface state density by $(NH_4)_2S_x$ treatment is also observed in the electronic properties of MIS capacitors. A significant improvement in the frequency dispersion of the MIS C-V characteristics is obtained by the treatment. Its interface state density is estimated from the 1 MHz C-V characteristics by Terman's method. In the case of GaAs, very low state density of 1 x 10^{11} $cm^{-2}\cdot eV^{-1}$ was successfully attained in the MIS structures, which were fabricated on the $(NH_4)_2S_x$-treated substrate using resistive-heating evaporated SiO_x.[4] All the results on the Schottky characteristics, the MIS C-V characteristics, and the MIS deep level transient spectroscopy (DLTS) measurement consistently indicate that the effect of $(NH_4)_2S_x$ treatment on many III-V compounds is a remarkable reduction in surface/interface defect density rather than a band bending caused by the presence of polar substances on the surface.

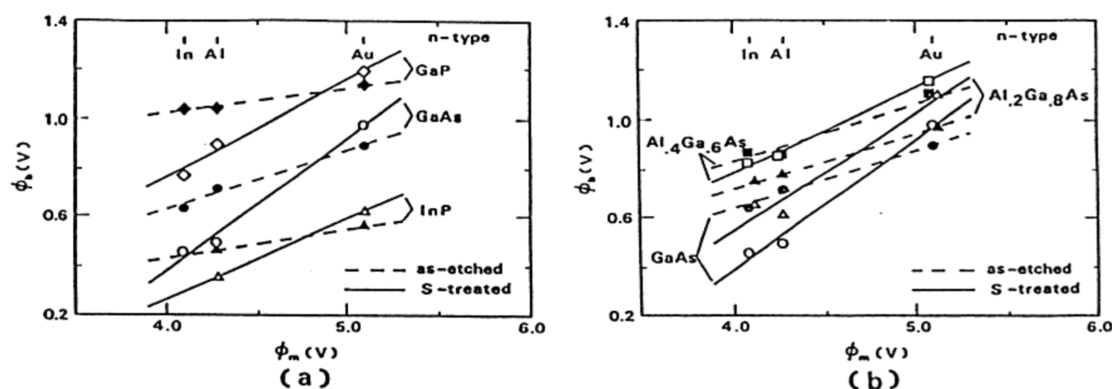

Fig. 1. Dependence of SBH on the work function of deposited metal. Schottky barriers were fabricated on the n-type (001) surfaces of various III-V compounds: (a) GaP, GaAs and InP, and (b) GaAs, $Al_{0.2}Ga_{0.8}As$ and $Al_{0.4}Ga_{0.6}As$.

A model for effectiveness of $(NH_4)_2S_x$ treatment

Combining all the surface analysis data obtained by AES, LEELS, PES, STM and RHEED, we propose a model to explain the effectiveness of the $(NH_4)_2S_x$ treatment, followed by a comparison with $(NH_4)_2S$ and Na_2S. For simplification, we explain only the case of well-studied GaAs, although our model is adaptable for many III-V compound semiconductors other than GaAs.[5] Figure 2 illustrates a model of GaAs surface with $(NH_4)_2S_x$ treatment.

The as-etched surface of GaAs is covered with a native oxide layer composed of Ga_2O_3 and As_2O_3 (Fig. 2(a)). The thickness of this layer is about 1 nm. Also observed is that cluster of elemental As, which is probably produced by a preferential formation of Ga oxide, is present in the oxide layer. We presume that interface region between oxide and GaAs is defective due to the off-stoichiometry of GaAs. When the as-etched sample is dipped into the $(NH_4)_2S_x$ solution, the oxide film is quickly etched away to reveal an oxygen-free surface of GaAs. Then the surface is instantly covered with reactive sulfur species such as S_x. This sulfurization reaction is considered not to produce the surface defects in GaAs because of the peculiarity of sulfur which nature is much different from that of other materials such as metals. For example, the sulfides of gallium and/or arsenic could form the layered structure. Since sulfides of GaAs dissolve in the alkaline solution of $(NH_4)_2S_x$, the reactions continue during a soak of the sample in it and thus the etching of GaAs layer resumes. This corresponds to the removal of surface defective layer of GaAs. The etching effect is also useful for flattening the surface. After the blown-dry process, a further precipitation of sulfur proceeds to form an amorphous layer (Fig. 2(b)). The amorphous layer of sulfur isolates the GaAs surface from the active atmosphere such as air. In vacuum, however, the amorphous layer of sulfur is so volatile that it sublimes and

disappears, leaving a monomolecular layer of sulfur on the top of GaAs. This indicates that sulfur atoms are chemically bonded with the GaAs surface.

The surface chemistry of sulfur was investigated in detail, by means of synchrotron radiation photoemission spectroscopy (SRPES).[6] On the as-treated surface of GaAs (Fig. 2(c)), some S-S bonds still remain, though most of amorphous sulfur quickly sublime in vacuum at RT. No oxygen atom is observed and As-S bonds are dominant. Ga-S bonds are barely observable or masked by the peak of As-S. By heating below 250 °C (Fig. 2(d)), S-S bonds disappear forming a monolayer of sulfur. A strong PES signal of As-S and a weak one of Ga-S are observed on the surface showing (1x1) structure. At higher temperatures above 250 °C (Fig. 2(e)), S atoms on the surface undergo the reconstruction by forming a (2x1) structure. This transition is characterized by disappearance of the dominant As-S bonds replaced by Ga-S bonds. Ga-S bonds are stable up to 520 °C. Above that (Fig.2(f)), S atoms gradually desorb to disappear from the GaAs surface.

Our interpretation for the effective surface passivation with sulfur is as follows. The etching effect of both native oxide and GaAs itself into the $(NH_4)_2S_x$ solution provide a defect-free surface, since it is considered that surface defects of the as-etched GaAs presumably concentrate at/near the interface of oxide/GaAs. Dangling bonds on this fresh/pristine surface are successfully terminated with sulfur atoms. As long as the surface is covered with sulfur, moreover, even very active oxygen is unable to chemically adsorb on GaAs. In other words, the surface of a monomolecular layer of sulfur is free from dangling bonds and so inert. According to the "advanced unified defect model (AUDM)" by Spicer *et al.*[7], this surface passivity of the sulfur-treated GaAs seems essential to the reduction in the interface state density. They have long proposed the AUDM for the origin of surface/interface states to explain the almost identical pinning position irrespective of the sort of adsorbed or deposited atoms. In their model, the pinning is introduced on (chemical) adsorption of foreign atoms or on deposition. The released energy to a substrate surface by chemical adsorption is sufficient to create the surface defects such as vacancy and antisite of As and/or Ga. Thus chemisorption of oxygen enhances in the SRV. In contrast to the chemisorption, the physicosorption may not have enough energy to create those defects. Therefore, we think that GaAs surface with sulfur is very effectively passivated and stabilized, because chemisorption to create the surface defects is prohibited on its dangling bond-free surface. This may produce the low interface state density of sulfur-passivated sample.

Another explanation could be related to the surface reconstruction. The structure of the $(NH_4)_2S_x$-treated (100) surface changes from (1x1) to (2x1) by the heat treatment.[8,9] This (2x1) diffracted pattern is due to the reconstruction of the surface involving S and Ga atoms. Furthermore, the upward band bending of n-type GaAs is relaxed by about 0.3 eV after the annealing.[6] This suggests that dominant formation of Ga-S bonds at the surface induces more decrease in the surface state density, which is consistent with the results calculated by an *ab initio* pseudopotential method. Ohno *et al.* explain this changes in surface characteristics from the results that density of antibonding states induced by As-S bond decreases with the heat treatment.[10]

Here we notice that treatment effect in our model is dependent upon the fabrication processes, *i.e.*, the degree of surface damage during the deposition. For Schottky contacts of nonreactive metals (In, Al, Au, *etc.*) with GaAs, the barrier height markedly varies approaching to the theoretical values assuming no defect density, while for reactive metals (Pd, Pt, *etc.*), the difference in SBH between as-etched and treated samples is not clearly recognizable.[11,12] Regeneration of surface/interface states might be related to the chemical reaction between metal and GaAs substrate. Moreover, the MIS structures fabricated by resistive-heating deposition are superior in electronic characteristics to those by electron-beam deposition, because the latter process involves the ion bombardment to the surface, resulting in the generation of surface defects.[4,13] We can see a similar behavior in the degradation rate of PL intensity. The as-etched surface of GaAs has a large SRV and rapidly degrades its PL intensity. On the other hand, the $(NH_4)_2S_x$-treated surface has a very slow degradation rate even after exposure to air, since its dangling-bond free surface hinders the chemisorption of oxygen, *i.e.*, oxidation.[14]

We also compare the $(NH_4)_2S$ and Na_2S treatment with $(NH_4)_2S_x$.[5] Because of the absence or a trace of the reactive sulfur species in $(NH_4)_2S$ solution, oxide removal and exposure of fresh GaAs is incomplete. Therefore, the coverage of GaAs surface with sulfur could be done only partially and the oxide could be left between GaAs and the sulfur layer. That is, the $(NH_4)_2S$ treatment is less effective. In the case of Na_2S treatment, the residue film seems to be Na_2S, as it is soluble in water. Once washed, the surface loses its improved properties. We interpret this phenomenon as follows: the Na_2S treatment leaves a polar film of $Na_2S{\cdot}9H_2O$ on the GaAs surface. The film could contain the space charge in it. The polar feature and/or space charge induce a band bending near the surface of

GaAs. In the Na_2S treatment, the defective surface layer of GaAs is left untouched, thus its real improving effect should be less significant than the $(NH_4)_2S/(NH_4)_2S_x$ treatment. In addition, once the film is washed away, the surface remains covered with the natural oxide as before the treatment. In other words, the passivation effect by the Na_2S treatment is almost founded on its polar or charged residual on the GaAs surface, though there might be a partial reduction in the defect density.

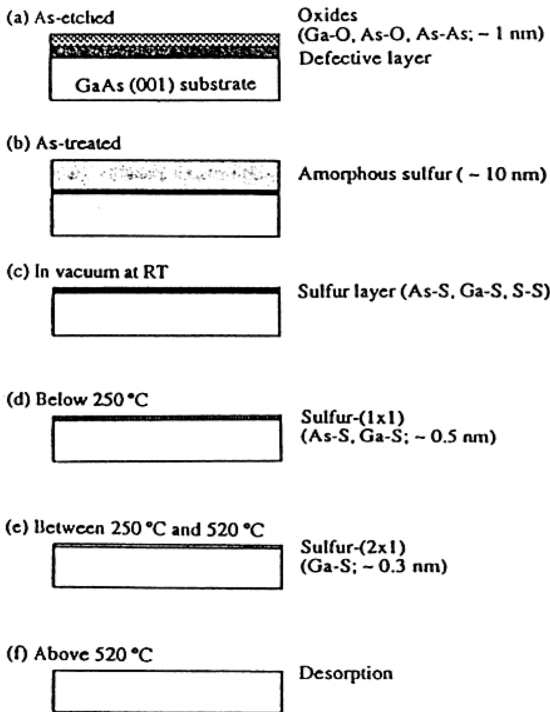

Fig. 2. Illustrative model of GaAs surface. (a) GaAs surface is covered with natural oxide, and defective layer of GaAs exists at/near the interface of oxide/GaAs. (b) Immediately after taken off the wafer out of the solution, the surface is covered with a visible, about 10 nm-thick film of amorphous S. (c) Most of amorphous S atoms quickly sublime in vacuum at RT, but some S-S bonds are observed as well as Ga-S in addition to the dominant As-S bonds. No oxygen atom is observed. (d) By heating below 250 °C, S-S bonds disappear and other bonds remain unchanged. The (1x1) RHEED pattern shows up. (e) Above 250 °C of transition temperature, Ga-S bonds become dominant on the (2x1) surface. (f) At higher temperatures above 520 °C, sulfur atoms gradually desorb to disappear from the surface. Sulfur atoms are losable by other means such as irradiation of light or electron beam.

Chalcogen treatment

We also studied on the surface passivation with chalcogen atoms (S, Se, Te). In these experiments, we used a dry process in stead of a wet process as $(NH_4)_2S_x$ treatment, due to a lack of effective solution for Se and Te treatment. An MBE technique was applied to control the molecular flux precisely and passivate the surface with chalcogen. The procedure of chalcogen treatment is as follows. The native oxide on the surface is removed with the heat treatment, and then the chalcogen flux is supplied on the clean surface at the substrate temperature of 480 °C. After shut off the flux, the substrate is cooled to RT. Schottky structures were fabricated on those surfaces at RT.

Figure 3 shows the SBH on GaAs passivated with S, Se and Te atoms. In general, SBHs of the chalcogen-treated sample have a larger dependency on the kind of metal than those of as-etched one, indicating a reduction in the interface state density. Therefore, the effect of chalcogen treatment seems quite the same on that of $(NH_4)_2S_x$ treatment, so long as a clean/fresh surface is attained prior to the treatment.

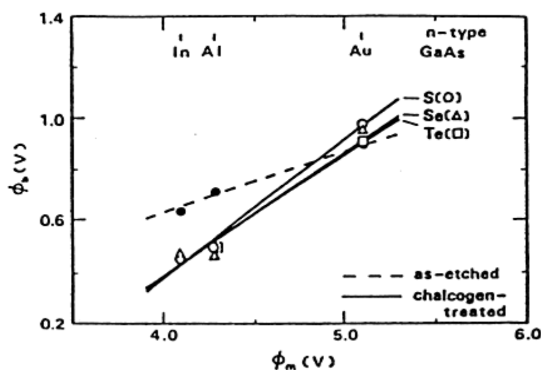

Fig. 3. Dependence of SBH on the work function of metal. The effect of Se and Te treatments is compared with that on S treatment.

Surface structure with chalcogen

Determination of the exact position of chalcogen atoms on top of the III-V surfaces is much sought after. We made observation on the various surfaces of S/InAs(001), Se/GaAs(001) and S/GaAs(111) by respective means of CAICISS, STM and XSW techniques, in order to avoid the technical difficulties in each measurement. In all those samples, however, we ascertained that the changes in bonding state of chalcogen with the heat treatment are qualitatively the same as S/GaAs(001).

The surface structure of $(NH_4)_2S_x$-treated InAs (001) was studied by CAICISS in combination with LEED and SRPES.[15] We used a sample of InAs to clearly separate the CAICISS signals between In and As, instead of GaAs with close atomic numbers. The intensity of back-scattered ions from In, As and S atoms were measured as a function of polar and azimuthal angles by using a time-of-flight (TOF) technique. In particular, we took notice of the behavior of S atoms with heat treatment and the actual displacement of S atoms involving surface reconstruction. CAICISS observations on the S/InAs(001) surface are as follows. The as-treated surface of InAs, on which exists both In-S and As-S bonds, has a less crystalline structure due to an abundance of As atoms. Based on the SRPES data that As-S bonds are predominant, this suggests that S atoms on the as-treated surface do not located on crystalline sites. On heating the sample at 380 °C, the surface morphology is gradually restored with the dominant formation of In-S bonds by the disappearance of As-S. In this condition, As atoms in the As plane of top surface are partially replaced by S atoms. The S or As atoms in the top layer form symmetric dimers lining up in the [$\bar{1}$10] direction, resulting in the (2x1) structure. Therefore, the surface reconstruction of (2x1) is explained by the formation of dimers involving sulfur atoms. At 430 °C, sulfur atoms on the InAs surface completely desorb, since InAs has the S-desorption temperature of 400 °C comparable to 520 °C for GaAs.

More detailed study was made by use of STM. We successfully observed the surface images of Se/GaAs(001)-(2x3) and (4x1) structures at an atomic level, since RHEED patterns progressively change to (1x1), (2x1), (2x3) and (4x1) with the heat treatment. When a GaAs(001) surface with Se adsorbates is flash-heated at c. 520 °C, the (2x3) RHEED pattern appears and remains even after the sample is cooled. Elliptical protrusions ordered with 0.6 nm periodicity in the [110] direction were observed. The distance between the rows aligned in the [110] direction was about 0.8 nm. A possible explanation of the structure is to attribute the elliptical images to the Se dimers. Se dimers which result from the replacement of As atoms by Se, were found to be buckled, but the 2x-periodicity was maintained in the [$\bar{1}$10] direction. Recent experimental results for bonding states suggest the formation of Ga-Se bonds at the Se/GaAs surface.[16] Figure 4 shows structural models for the Se/GaAs(001)-(2x3) surface.[17] Such a structure may be stabilized through charge transfer of the excess electrons into the Ga dangling bond states which appear by desorption of chalcogen atoms. Further heating at slightly higher temperature (~530 °C) produces the (4x1) surface structure of Se/GaAs(001). STM images revealed the presence of ordered arrays with regular intervals of 4x-periodicity in the [$\bar{1}$10] direction (1.6 nm) lining up in the [110] direction. In a closer view, we also found that the 4x structure is formed by closely placed double rows. Although mechanisms to explain the formation of 4x-structure are under consideration, the reconstruction such as dimer paring may be caused by the partial replacement of As atoms by Se in the surface layers.

Furthermore, the coherent position of sulfur atoms were determined on the (111)A and B surfaces of $(NH_4)_2S_x$-treated GaAs by means of XSW technique.[18] The $SK\alpha$ fluorescence yields generated by the GaAs(111) standing waves were measured by a UHV goniometer system. The $SK\alpha$ fluorescence angular yield of the as-treated surface demonstrated that S atoms are located in nearly random positions on the surface, where Ga-S, As-S and S-S bonds coexist. This feature is common to both S/GaAs(111)A and B surfaces. After annealing, the S atoms substitute with top As atoms and occupy the coherent position of $0.89 \cdot d_{111}$ for (111)A and $0.00 \cdot d_{111}$ for (111)B, where $d_{111} = 3.264$ A is the spacing of the GaAs(111) planes. In other words, S atoms on the GaAs(111)A surface are located on top of the first layer Ga atoms, and bonded to the Ga atoms. This makes a sharp contrast to the (111)B surface, where the S atoms replace the first layer As atoms, and each S atom is bonded to three Ga atoms in the second layer. One may expect that the desorption temperature of S atoms on (111)A surface differs from that on (111)B, based on the idea that sulfur coordination number ranges from 1 for (111)A to 3 for (111)B. In fact, the temperature at which S atoms completely disappeared is 580 °C and 618 °C for the (111)A and B surfaces, respectively. This result was obtained by SRPES measurements.[19]

XSW technique is also useful to determine the position of interfacial atoms, though it is impossible to measure all the samples with various crystal orientations. With the help of XSW, we

investigated the structure of S atoms which exist at each interface of CaF_2-, Al- and Pd-GaAs(111)A·B.[20,21] We found that in the case of CaF_2 and Al, the interfacial S atoms are well-ordered even after the deposition, while those in Pd are rather disordered. The results observed by SRPES revealed the presence of Ca-S and Al-S bonds at the interface with CaF_2 and Al, respectively. As for Pd, however, Pd-Ga-As bonds are observed instead of Pd-S bonds. In fact, no significant difference in SBH between with and without the treatment was observed. As described before, the treatment effect is completely lost on the Pd/S/GaAs system because of the collapse of passivating S layer during the deposition.[12] In addition, the samples with (111)A have a lower coherent fraction than those with (111)B, meaning a less ordering of (111)A samples. This corresponds to the result that Ga-S bonds on (111)A are weaker than that on (111)B. Hence, we think that the existence of chalcogen-related bonds at the surface/interface provides the passivation effect on the III-V compounds.

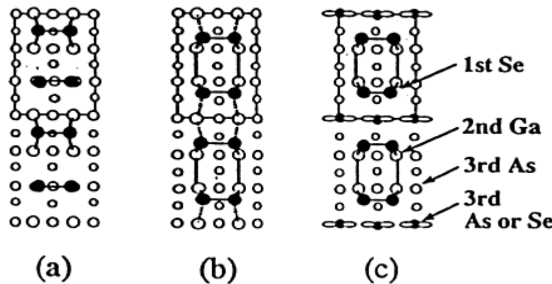

Fig. 4. Structural models for the Se/GaAs(001)-(2x3) surface.

Oxidation of chalcogen-passivated surface

The passivation effect with chalcogen is attributable to the formation of III-chalcogen bonds at the surface, in which the dangling bonds of III elements are successfully saturated. However, the chalcogen-passivated surface is not sufficiently stable against a long exposure over 10 days to air and a light irradiation. So we examined the cause of degradation observed on the air-exposed or light-irradiated surface with SRPES and positron annihilation technique.[22,23] Information obtained from the positron annihilation is about the presence of positron trapping center which has a negative charge. Among the six kinds of point defects possible in GaAs, positron is only sensitive to the acceptor-type vacancies such as V_{Ga} and/or V_{Ga}-related defects. That is, the donor-type V_{As} and antisites such as Ga_{As} and As_{Ga} have no trapping potential for positron.

In course of SRPES measurements, we found that the S-passivated GaAs surfaces which consist of 1 to 2 ML Ga-S layers comparatively protect and inhibit the surface oxidation. However, exposure to air induces the oxidation of Ga first and then As through the Ga-S layer, resulting in the degradation of surface electronic properties. This is based on that Ga oxide is thermodynamically more stable than As oxide. The preferential formation of Ga oxide is considered to generate the vacancy of Ga and excess elemental As. Nevertheless, the presence of V_{Ga} at the near-surface region could not be found by positron annihilation measurements. These results tentatively suggest an occurrence of the defect reaction; $V_{Ga} + As_{As} \rightarrow V_{As} + As_{Ga}$. This argument is founded on the theoretical calculations that enthalpy of antisite formation is much lower than that of vacancy formation.[24] An increase in the surface defects caused by the oxidation procedure results in a drastic upward band bending, approaching to the main pinning level of As_{Ga} antisite defects. Accordingly, the predominant defect at the GaAs surface might be considered to be the V_{As}-As_{Ga} complex created by the chemisorption of oxygen.

Summary

We found a very effective surface treatment of III-V compound semiconductors with the $(NH_4)_2S_x$ solution of excess sulfur. This treatment removes the natural oxide, etches III-V compounds and covers the surface with a monomolecular layer of sulfur. Moreover, the sulfur layer is so inert that the foreign atoms can not adsorb chemically. Our model suggests that these phenomena produces a well-stabilized surface and suppresses the regeneration of surface defects. In fact, the significant effect of $(NH_4)_2S_x$ treatment was observed as follows: 1) enhancement in PL intensity; 2) clear dependence of SBH on the work function of metal; 3) improvement in C-V characteristics of MIS structures. The latter two effects mean the real reduction in the surface/interface state density rather than band bending. Heat treatment of the as-treated surface is essential to stabilize

more effectively its surface. This is due to the dominant formation of III-S bonds which is stabler than V-S bonds, since III-S and V-S bonds coexist on the as-treated surface.

The effects of S-treatment were extended to those of other chalcogen (Se and Te) treatment. Similar dependency of SBH on the sort of metal was clearly observed. Therefore, we think that the effect of chalcogen (S, Se, Te) treatment is almost universal on the surface of many III-V compounds. On the as-treated surface, the V-chalcogen bonds are predominantly formed, resulting in the broken III-V bonds. Consequently, the surface indicates a less crystalline structure due to an abundance of V atoms. After annealing the samples, the partial replacement of V atoms by chalcogen and the subsequent formation of III-chalcogen bonds occur at a few layers of the surface. This behavior agrees with that III-chalcogen bonds are thermodynamically stabler than V-chalcogen bonds.

We also clarified the surface structure of chalcogen-passivated samples on an atomic scale, by the use of CAICISS, STM and XSW techniques. Chalcogen atoms occupy the near-site of V elements on top of the surface. This behavior seems to be independent of the surface orientation, although the chalcogen dimer rows are observed on the (001) surfaces. Structural models for Se/GaAs(001)-(2x3) were presented, based on the elliptical STM images corresponding to the Se dimers on the Ga layer.

Though a full understanding of the mechanism of chalcogen passivation is not reached yet, we extend that the effect and structure is qualitatively the same on the surface of III-V compound semiconductors.

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