Ultrathin (1×2)-Sn layer on GaAs(100) and InAs(100) substrates: A catalyst for removal of amorphous surface oxides

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Amorphous surface oxides of III–V semiconductors are harmful in many contexts of device development. Using low-energy electron diffraction and photoelectron spectroscopy, we demonstrate that surface oxides formed at Sn-capped GaAs(100) and InAs(100) surfaces in air are effectively removed by heating. This Sn-mediated oxide desorption procedure results in the initial well-defined Sn-stabilized (1×2) surface even for samples exposed to air for a prolonged time. Based on *ab initio* calculations we propose that the phenomenon is due to indirect and direct effects of Sn. The Sn-induced surface composition weakens oxygen adsorption. © *2011 American Institute of Physics*. [doi:10.1063/1.3596702]

Amorphous (or polycrystalline) oxide layers are easily formed at the surfaces of III–V semiconductors exposed to oxygen. The formation of such structurally and electronically poor III–V oxide layers is detrimental for the development of many types of devices. Detrimental effects include surface Fermi-level pinning in the III–V channel of metal-oxide-semiconductor field-effect transistors (MOSFETs), increased surface recombination, barrier formation within metal-semiconductor contacts, and surface contamination affecting regrowth processes. The first example is probably the best known; the formation of amorphous surface oxides at the interface between a III–V semiconductor and an insulator causes the Fermi level to pin via defect states, thus rendering the development of III–V channels difficult for practical MOSFETs. A significant effort has therefore been made to understand how III–V oxides can be removed (or their formation prevented) during the fabrication of insulator–III–V junctions.[1–12] However, it is still unclear whether it is possible to avoid the oxygen reaction during interface growth, and there is still much room to improve insulator–III–V interfaces and our overall understanding of III–V oxidation. Simultaneously, an increasing number of studies[5,13–19] has revealed the importance of atomic-scale information and of the processing of semiconductor surfaces, so-called surface engineering, for controlling the properties of the semiconductor interfaces. These studies have shown that a properly chosen thin adsorbate layer with a well-defined structure significantly improves the properties of oxide-semiconductor interfaces for various types of semiconductor devices.

In this letter, we report an interesting effect of Sn-capping on the desorption properties of amorphous oxides of GaAs(100) and InAs(100) surfaces. In particular, we have found that the initial Sn-stabilized (1×2)-ordered GaAs and InAs surfaces, comprising 0.5–1.0 monolayer (ML) of Sn, can be restored even after a week's exposure to air; in other words, the native surface oxides formed can be efficiently removed by heating the substrates in a vacuum. This property may be useful not only for the development of the long-sought III–V MOSFETs but also for example for the development of Ohmic contacts and re-growth applications.

Deposition of 0.5–1 ML of Sn and postheating (500 °C for GaAs and 300 °C for InAs) produced clear low-energy electron diffraction (LEED) patterns. Details of the experiments have been described recently.[20] The reference (without Sn) and Sn-covered substrates were exposed to air in an open loading chamber and in a separate air-filled cabinet. Photoemission measurements were performed at the MAX-laboratory beamline 41 (Sweden), using a synchrotron source and at the home laboratory, using an Mg K_α (1253.6 eV) x-ray source. Details of our room temperature measurements can be found elsewhere.[21–23]

The photoemission and LEED measurements for the samples exposed to air are summarized in Fig. 1. Figure 1(a) shows a clear difference in Ga 3*d* emissions between the GaAs(1×2)-Sn and the pure GaAs-*c*(8×2) surfaces after air exposure and postheating. The Ga 3*d* of the air-exposed GaAs-*c*(8×2) is broadened due to Ga oxide emission, and shows a band-bending-related energy shift as compared to the clean GaAs-*c*(8×2). This observation is consistent with the appearance of the O 1*s* emission [Fig. 1(b)]. LEED measurements for the air-exposed GaAs-*c*(8×2) revealed a poor (1×1) pattern, which was not improved after prolonged heating. In contrast, the Ga 3*d* emission from the heated GaAs(1×2)-Sn surfaces does not present any oxide-related

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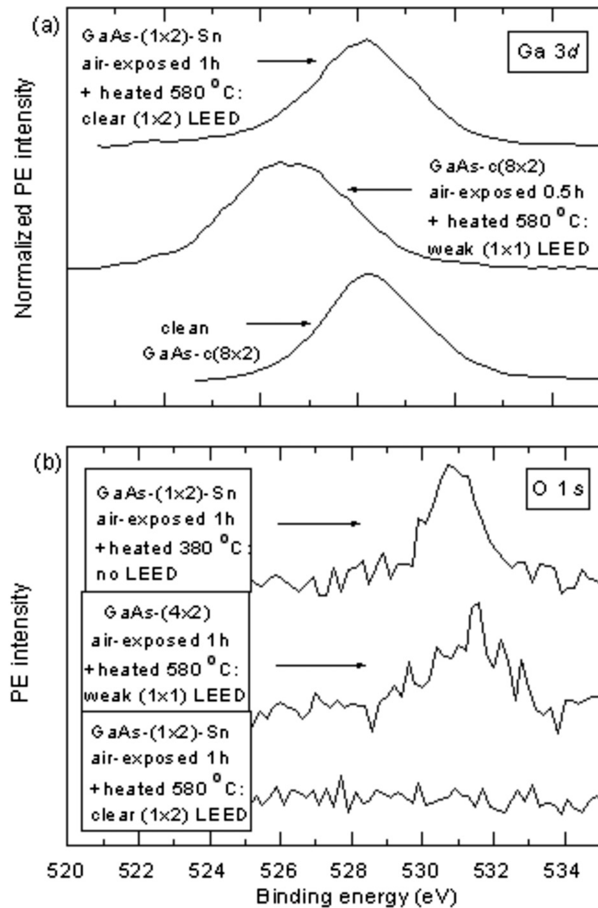

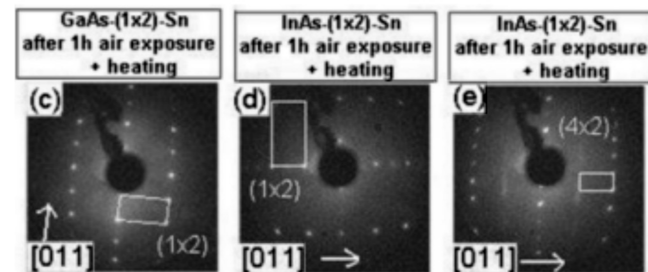

FIG. 1. (a) Ga 3*d* emissions from GaAs(1×2)-Sn (top) and pure GaAs-$c(8\times2)$ (center) after air exposure and annealing in vacuum, and from pure GaAs-$c(8\times2)$ before air exposure (bottom). (b) O 1*s* emissions from GaAs(1×2)-Sn (bottom and top) and GaAs-$c(8\times2)$ (center) after air exposure and annealing at different temperatures. (c) LEED (120 eV) from GaAs(1×2)-Sn after 1 h air exposure and 0.5 h annealing at 550 °C, showing a clear (1×2) pattern. (d) LEED (57 eV) from InAs(1×2)-Sn after 1 h air exposure and 0.5 h annealing at 450 °C, showing a clear (1×2) pattern. (e) LEED (55 eV) from InAs(1×2)-Sn after 1 h air exposure and 0.5 h annealing at 470 °C, showing a clear $c(8\times2)/(4\times2)$ pattern.

broadening or band bending, consistently with the absence of O 1*s* emission [Fig. 1(b) bottom]. Moreover, the GaAs(1×2)-Sn surface exhibited a sharp LEED [Fig. 1(c)] after air exposure and heating. Even after air exposure for one week, the GaAs(1×2)-Sn produced a clear (1×2) LEED after heating to 580 °C; at the same time the Ga 3*d* peak did not include the oxide emission. The LEED from samples exposed to air for a week was of course not as sharp as in Fig. 1(c) but the quality of the pattern improved with prolonged heating. It is important to note that after air exposure but before any heating, both the GaAs(1×2)-Sn and the pure GaAs-$c(8\times2)$ samples exhibited a poor (1×1) LEED and Ga oxide emissions. The InAs(1×2)-Sn behaves in the same way as the GaAs(1×2)-Sn after air exposure but it has some unexpected properties as follows: Sn re-evaporated from the InAs more easily than from the GaAs since heating to 470 °C removed Sn from the InAs and produced the pure InAs-$c(8\times2)$ surface [Fig. 1(e)] while the (1×2)-Sn remained on the GaAs at least up to 600 °C. Our preliminary tests show that InSb(100)-Sn system behaves like the InAs(100)-Sn.

Figure 2 shows high-resolution photoemission spectra from InAs(1×2)-Sn before and after air exposures and also after heating the air-exposed samples. The same measurements of GaAs(1×2)-Sn reveal the behavior (not shown) similar to that in Fig. 2. The high binding energy (BE) components S^* clearly indicate that the GaAs and InAs substrate surfaces are oxidized during air exposure.[24,25] It also appears that As oxides are the first oxides to be removed by heating. The Sn 4*d* spectra also reveal many surface components S^* and S^{**} at higher BE than the InAs(1×2)-Sn peaks; this agrees closely with previous reports, showing similar peaks between 1.5 and 2.5 eV measured from SnO and SnO_2 compounds.[26]

To interpret the experimental findings, *ab initio* calculations were performed using the projector augmented wave method as implemented in the Vienna *ab initio* Simulation Package.[27,28] The plane wave cutoff energy was set at 400 eV. The computation procedure is described elsewhere.[20,29] The adsorption of an oxygen atom was simulated for different surfaces, including $c(8\times2)$, $\beta(2\times4)$, and Sn-induced (1×2). Several relevant surfaces were considered to rule out the possibility that the results were dependent on the surface chosen or on the position of the oxygen atom. One substitutional Sn atom was inserted into the $c(8\times2)$ and $\beta(2\times4)$ reconstructions while on the Sn-stabilized surface Sn coverage varied between 0.125 and 0.625 ML. The Ga and As atoms in the first and second layers of GaAs-Sn were gradually substituted by equivalent Sn atoms, and several different relatively stable adsorption sites were considered. Local Sn clustering was also tested. The (4×2) unit cells adopted enabled the comparison of similar oxygen adsorption sites with different nearest-neighbor environments. The total energy results show consistently, regardless of surface or Sn coverage, that by replacing a Ga/In (As) atom with a Sn atom the adsorption/desorption energy of a neighboring O atom is decreased (increased) by 0.1–0.8 eV (most of the shifts are within 0.4 eV); in other words, it is easier (more difficult) to desorb oxygen. The tendency observed is thus probably also valid on a more or less disordered surface which is relevant, because surface is reconstructed upon oxidation. The results are in agreement with the experimental observation according to which As oxides are the first oxides to be removed by heating. If some of the Ga/In atoms are replaced by Sn atoms, the surface tends to desorb oxygen more easily. We recall that the GaAs surface is crystallized in the ζ-$c(8\times2)$-structure[29] in Ga-rich conditions at 0 K (although under finite temperatures there are also ζa-type areas on the surface[30,31]), and the number of Ga atoms in the surface layer is slightly reduced in the Sn-induced phase transition to the (1×2) reconstruction. The absolute value of the adsorption energy depends strongly on the adsorption position (scatter in adsorption energy is more than 1 eV), which is a common result for all surfaces considered.

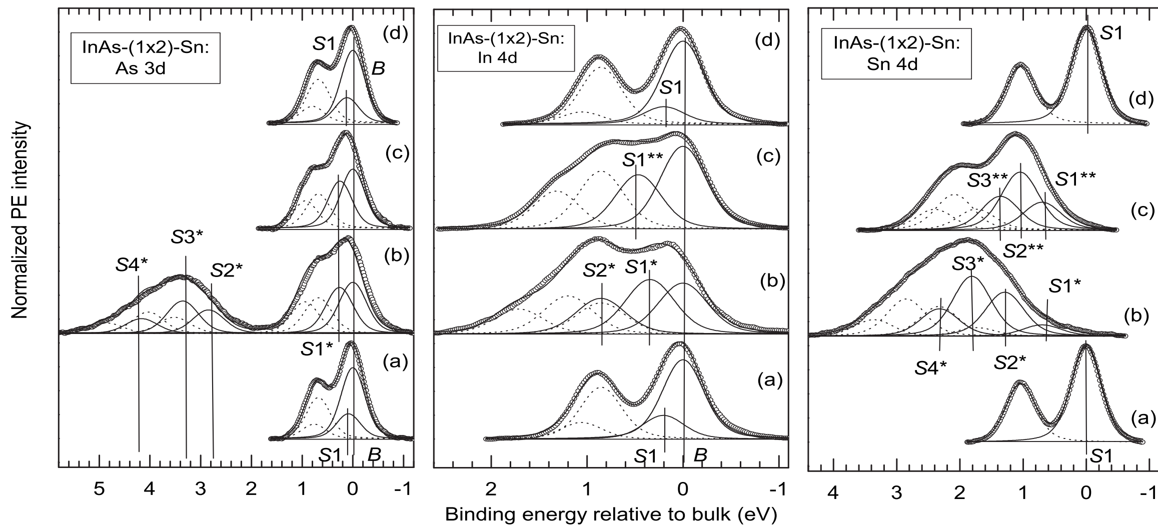

FIG. 2. As $3d$, In $4d$, and Sn $4d$ photoemissions from InAs(1×2)-Sn (a) before air exposure, (b) after air exposure, and [(c) and (d)] after heating of the air-exposed sample at 420 °C and 450 °C, respectively. The spectra were fitted with the minimum number of components. B represents InAs bulk components; different S components are surface-related. Sn $4d$ spectra were aligned with In $4d$ bulk components.

As the Sn coverage on the (1×2) surface is only around 0.5 ML, and not many Ga (In) atoms are replaced with Sn atoms in the Sn-induced reconstruction change, we suggest that the Sn-induced surface structure/composition change has a great effect on oxygen desorption. (Most favorable adsorption sites are within the surface layers.) Sn adsorption induces the (1×2) reconstruction, in which there are only four Ga (In) atoms in the surface layer and no Ga (In) atoms in the second layer of the (4×2) surface area. On the other hand, the ζ-$c(8\times2)$ [ζa-$c(8\times2)$] unit cell of the III–V compound comprises six (eight) Ga (In) atoms in the more dense III–V mixed surface layer and eight Ga (In) atoms in the second layer of the (4×2) surface area. Thus there will be much more relatively strong Ga–O bonds within the surface layers of pure GaAs upon oxidation compared to Sn/GaAs. There are also adsorption positions in the second layer of the $c(8\times2)$ structure which have a peculiarly large BE, because in these positions the O atoms are bound only to group III atoms. In the (1×2) structure the most favorable oxygen position is on top of the Ga(In)-Sn dimer in the surface layer, which may also facilitate oxygen desorption. The energy difference between the most favorable adsorption positions in the (1×2) and ζ-$c(8\times2)$ [(1×2) and ζa-$c(8\times2)$] reconstructions is about 0.2 eV [0.5 eV].

To recapitulate: the (1×2)-Sn layer did not prevent substrate oxidation and the formation of an amorphous surface layer in air, but significantly improved the removal of surface oxides (enabled effective surface cleaning with heating of the samples). Our results agree with, and may also provide a partial explanation for, the beneficial effects of Sn on III–V(100) surfaces;[32–35] the deposition of an Sn prelayer in the epitaxial growth of GaAs effectively eliminates interfacial defects.[32] Furthermore, an Sn submonolayer has been found to act as a surfactant in GaAs epitaxial growth.[33] Sn is also an n-type dopant of III–Vs, and Sn-terminated growth fronts have been found to affect bulk doping concentrations.[35] Recent studies[20,36] have elucidated the atomic structures of the (1×2)-Sn surfaces.

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