GaSb-oxide removal and surface passivation using an electron cyclotron resonance hydrogen source

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We describe the use of a low-temperature technique, which is based on H atoms from a microwave electron cyclotron resonance (ECR) H_2 plasma, to remove surface oxides and carbon from a single-crystal GaSb surface. Our experiments indicate that oxide removal occurs at a temperature of ~250 °C, much lower than that for thermal evaporation of the oxide. In addition, we have found that subsequent exposure to N atoms from a N_2 plasma leaves a thin nitride layer, which prevents degradation of the H-cleaned surface. To demonstrate this technique, we have applied it to the processing of an AlGaSb PIN photodiode, which is fabricated with molecular-beam epitaxy material. Our electrical measurements show that the leakage current, after surface Sb-oxide removal, is significantly reduced from that before the ECR-H treatment.

I. INTRODUCTION

Electron cyclotron resonance (ECR) plasmas offer many important advantages for semiconductor processing, including low ion energies (10–20 eV), and thus low surface damage; and relatively high electron densities, and thus high processing efficiency. Its low pressure operation and simple design make the technique compatible with ultrahigh vacuum (UHV) integrated processing.[1,2] These advantages are of particular importance for compound semiconductor processing because of the need for low-temperature *in situ* surface preparation.

In particular, GaAs surface cleaning by H atoms from an ECR hydrogen plasma has been used previously for *in situ* sample preparation of wafer surfaces before MBE growth.[3–7] This technique has been used to prepare a clean and ordered GaAs surface at relatively low sample temperatures (~250 °C). In addition, it was found that ECR-hydrogen plasma-cleaned surfaces have much less residual carbon. Subsequent growth leads to an interface with minimal carrier depletion.[3–5,8] Exposure to a hydrogen plasma, including an ECR-H plasma, has also been reported to passivate temporarily the GaAs surface and the outer portions of the bulk wafer.[9–18]

Recently there has been increasing interest in other gallium-containing semiconductors for quatum-well (QW) devices. Specifically, GaSb-based material structures have received added emphasis because of their flexibility in band gap design and their ease of epitaxy. These attributes have been shown, for example, in low-noise avalanche photodiodes, ultrafast resonant-tunneling diodes, etc.[19] However, there has been a paucity of studies on practical surface preparation procedures, particularly with regard to low-temperature techniques for oxide removal and passivation.

In this article, we will describe the use of atoms from a low-temperature microwave ECR plasma to prepare a clean surface of GaSb; the study uses x-ray photoemission spectroscopy as the main diagnosis tool. Using this tool, we have developed specific low-temperature techniques for removing surface oxide, and for subsequently protecting the surface. In addition, we have applied this technique to the surface passivation of a GaSb-based photodiode. As a result of this treatment, the leakage current of the diode has been significantly reduced.

II. EXPERIMENTAL

The experiments were carried out in an UHV system with two independent chambers. These chambers are equipped with a monochromatic x-ray photoelectron spectroscopy (XPS) system using an Al $K\alpha$ source, in the analysis chamber, and a residual gas analyzer (RGA), and a custom-made ECR source, in the sample treatment chamber. The ECR plasma is excited with a 120 W, 2.45 GHz microwave source. A 1.5 in. diam quartz cell on the UHV system, surrounded by a microwave cavity and an electromagnet, allows the microwaves to be absorbed by the gas in an 875-G magnetic field. The process gas is introduced at the base of the quartz cell, and the typical chamber pressure is 5×10^{-4} Torr for nitrogen, and ~1 mTorr for hydrogen. The gas diverges out of the plasma region to form a uniform, broad source. Samples are positioned ~20 cm from the center of the plasma region where they are exposed to the various downstream plasma products consisting of atoms, undissociated molecules, electrons, and ions; of these species we believe that the dominant reactive constituent is H atom. Light emitted from the plasma source also impinged on the sample. The hydrogen ECR plasma ion density was measured using a Faraday cup. The saturation current was determined to be $I_{sat} = 400$ nA/cm^2 for hydrogen at 60 W of absorbed microwave power.

The sample could be biased to eliminate selectively positive or negative particles from being incident on the sample in order to allow modification of the reaction conditions. In the case of the hydrogen plasmas, a low bias (-2 V) was used in order to determine whether the plasma was established, since the bias caused a small ion current to pass through the sample when the plasma was present.

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This procedure was required because the small amount of visible light emitted from our low pressure hydrogen plasma made optical confirmation of plasma ignition difficult.

Research grade hydrogen and nitrogen were used, and the purity of the gas was checked by a RGA. Both GaSb (100) and (111) orientation samples were used in our experiments. All surfaces were chemically precleaned by using NH_4OH. The precleaned sample was loaded into the UHV system, which had a base pressure $\sim 1 \times 10^{-8}$ Torr in the sample treatment chamber and $< 3 \times 10^{-10}$ Torr in the sample analysis chamber.

XPS spectra of the Sb $3d$, Ga $2p_{3/2}$, Ga $L_3M_{4,5}M_{4,5}$ (Auger transition), and the C $1s$ core levels were normally taken before and after ECR processing. Under the typical XPS data acquisition conditions, the Au $4f_{7/2}$ peak at 84.0 eV binding energy (BE) had a width [full width at half-maximum (FWHM)] of 0.8 eV. The run-to-run energy position resolution was within ± 0.1 eV. The analyzer settings and acquisition time for each run were kept constant in order to make meaningful comparisons of peak areas, which correspond to elemental concentration.

III. RESULTS AND DISCUSSION

Thermal desorption of GaSb oxide has been studied previously and the oxide desorption temperature determined to be between 480–510 °C.[20] Before beginning our plasma experiments, we wished to examine this thermal reduction more carefully and to observe, in particular, the thermal chemistry at temperatures less than this desorption temperature. For these lower temperatures, important phenomena, such as the thermal reaction products and the temperature range of thermal desorption for Sb oxide, could be observed directly. Data summarizing our thermal reaction experiments are shown in Fig. 1. In this experiment, a GaSb sample, covered with both Sb oxide and Ga oxide, was loaded and examined by XPS. The sample temperature was then raised to a predetermined value, held at this temperature for a fixed time interval, and then, after cooling to room temperature, an XPS measurement was again taken. In these spectra, both spin–orbit split branches of Sb $3d_{5/2}$ and Sb $3d_{3/2}$ have an additional peak positioned at a higher binding energy relative to its substrate peak, indicative of the Sb–O chemical shifted peak. The shift toward higher binding energy is consistent with the electronegativity of the oxygen atom.

As shown in Fig. 1(a), with simple substrate heating, Sb oxide begins to lose its intensity significantly at around 340 °C, and, in fact, is completely eliminated when the temperature goes above 435 °C. However, when the sample was heated to between 250 and 500 °C, the Ga-oxide intensity increased as a function of temperature, as shown in Fig. 1(b). This observation was made by use of the Auger Ga-$L_3M_{4,5}M_{4,5}$ transition, which has a separable chemical shift ($\Delta E = 3.8 \pm 0.1$ eV) for the Ga in Ga-oxide versus the Ga in GaSb.[21] Since the oxide elimination took place over a wide temperature range, an explanation via a simple desorption process does not seem suitable. The reaction mechanism may be analogous to that which occurs during thermal annealing of the oxide of GaSb, as originally proposed by Schwartz *et al.*[22] In this case, near the GaSb interface Sb_2O_3 is reduced, giving rise to Ga_2O_3 and metallic Sb via the reaction $Sb_2O_3 + 2GaSb \rightarrow Ga_2O_3 + 4Sb$. Later, the pure Sb outdiffuses thermally reaching the surface. The pure Sb presumably evaporates from the surface.

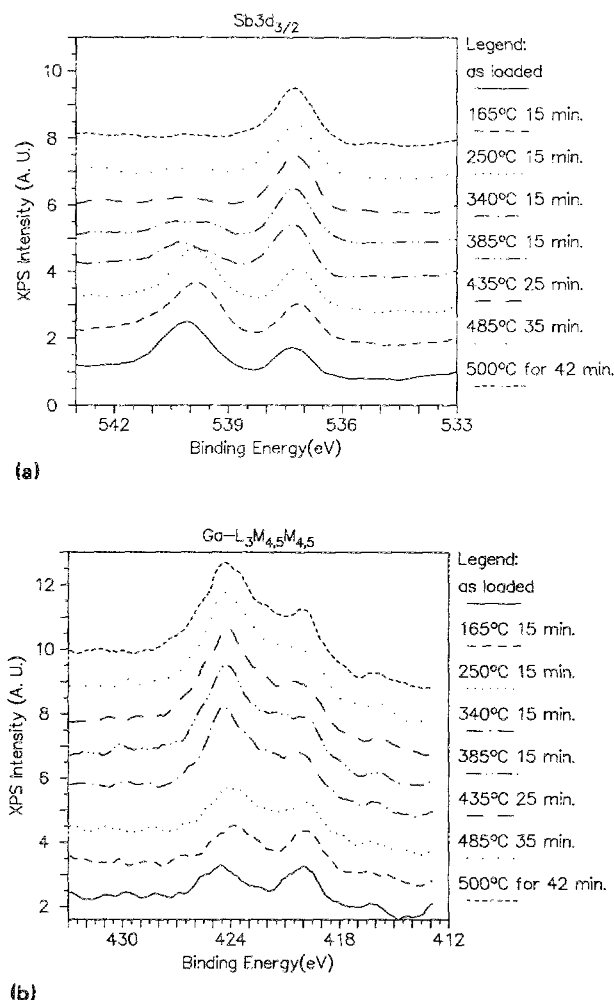

FIG. 1. XPS spectra of an oxidized GaSb surface heated in vacuum at different temperature and for different time intervals. (a) Sb $3d$ core level, (b) Ga-$L_3M_{4,5}M_{4,5}$ Auger transition.

The plasma experiments were done by exposing the samples to the discharge products in the preparation chamber of the monochromatic XPS system; samples are then transferred into the analytical chamber. Using this system, we find that at room temperature the Sb oxide, as well as any carbon, on the GaSb surface can be completely removed by a 30 min exposure to an ECR hydrogen plasma. The XPS spectra of the Ga $2p_{3/2}$, Sb $3d$, and C $1s$ core levels for a GaSb sample before and after ECR-H treatment are displayed in Fig. 2. Detailed nonlinear curve fitting for both the Sb $3d_{3/2}$ core level and the Ga $2p_{3/2}$ core level show that Sb oxide appears in both the $+3$ (Sb_2O_3), and $+4$ (Sb_2O_4) valence forms and that the Ga oxide is in the $3+$ state (Ga_2O_3). Their peaks are positioned 2.4 ± 0.1 eV, 3.2 ± 0.1 eV, and 1 ± 0.1 eV higher in binding energy, respectively, with respect to their substrate positions. As shown in the *in situ* XPS measurement, the

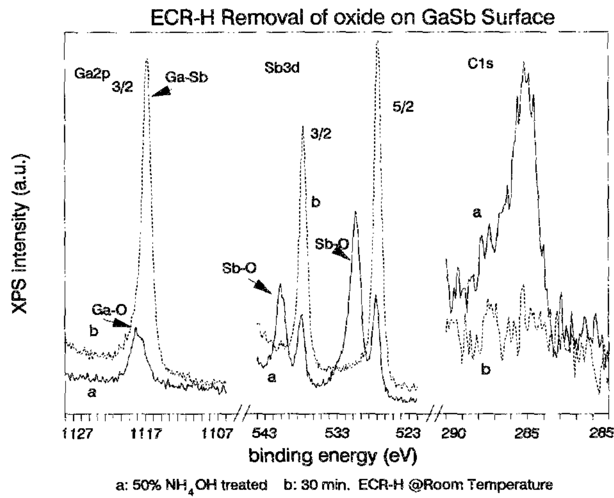

FIG. 2. XPS spectra of the Ga $2p_{3/2}$, Sb $3d$, C $1s$ core levels for a GaSb surface (a) chemically cleaned (solvent cleaning plus 50% NH_4OH for 1 min); (b) after exposure to a 30 min ECR-H plasma at room temperature.

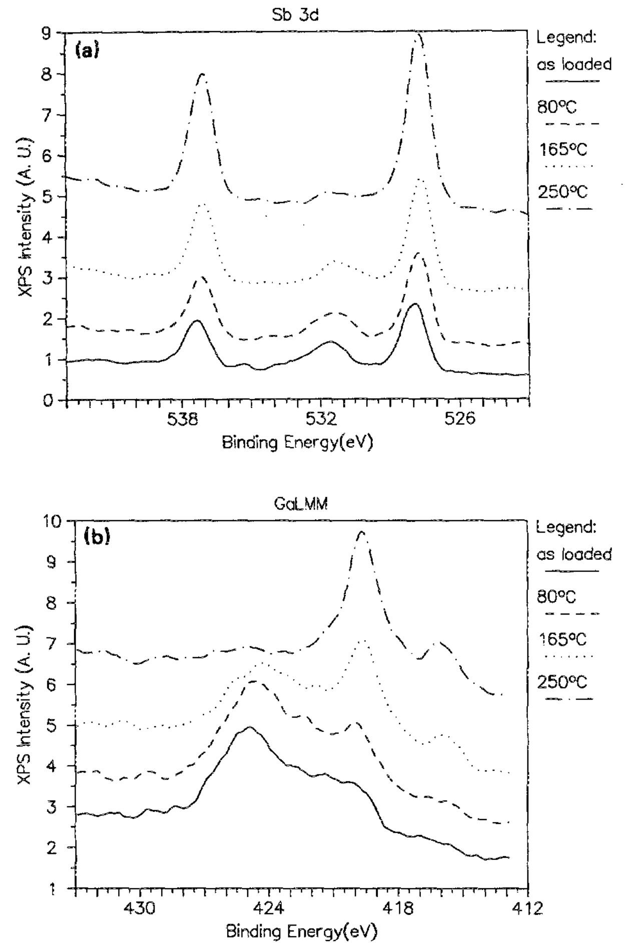

FIG. 3. GaSb surface exposed to ECR-H plasma at different temperature for 20 min (a) XPS spectra of the Sb $3d_{3/2}$ core level; (b) XPS spectra of the Ga-LMM Auger transition.

Sb-oxide and carbon traces disappear completely after ECR hydrogen treatment, whereas the Ga-oxide trace is reduced. The significant increase of the unshifted substrate Sb $3d$ and Ga $2p_{3/2}$ core-level intensities is also consistent with the oxide overlayer removal. The incomplete reduction of the Ga oxide is consistent with the fact that the Ga oxide has a much higher free energy of formation than does Sb oxide.[23] Additional exposure of the GaSb sample to an ECR-H plasma for 1 h at room temperature was still insufficient to fully remove the Ga oxide. The removal of the Sb oxide and free carbon is attributed to the ready formation of volatile species from atomic hydrogen, such as H_2O and hydrocarbon, in the vacuum chamber.

Experiments were also carried out to further examine the temperature at which Ga oxide could be reduced by the ECR hydrogen plasma. The XPS spectra of the GaSb sample, with the initial layer of Ga oxide exposed to different temperatures for 20 min intervals, are displayed in Fig. 3. In the Sb $3d$ spectra, both spin–orbit components, Sb $3d_{5/2}$ and Sb $3d_{3/2}$, are shown. Note that a peak at binding energy 531.5 eV is due solely to O $1s$, not oxide shifted Sb $3d$ core level. For this peak to be due to Sb oxide there would have to be a companion Sb $3d_{3/2}$ feature, as is seen in Fig. 2. Thus, this starting surface apparently has only Ga oxide. As was seen earlier, the Ga oxide was difficult to remove from a sample at room temperature. Measurements at intermediate temperatures indicated that heating to approximately 250 °C was necessary to achieve a complete reduction of Ga oxide for a 20 min processing time. While the preparation of a clean GaSb surface requires complete removal of both Sb oxide, Ga oxide, and carbon, in certain passivation applications to be discussed below, removal of Sb oxide is itself a useful procedure. In this case, a simple room-temperature H plasma is sufficient. To achieve room-temperature reduction of Ga oxide, one must significantly improve the percentage of atomic hydrogen generated in the plasma. This improvement may be realized by using a noble gas (He or Ar) additive to the H_2 plasma. Our preliminary results, shown in Fig. 4, indicate that Ga oxide can be reduced at room temperature by a hydrogen and He mixture (He/H_2:3/1). Further, experimental investigation is needed to find the best gas mixture ratio for achieving the maximum oxide reduction rate at room temperature.

In some cases, H-terminated semiconductor surfaces have been found to remain passive over a long period of exposure to air.[24] In order to determine the longevity of the H treatment, air exposure of an ECR-H cleaned GaSb surface was measured with XPS; the result is shown in Fig. 5. In this experiment, an ECR-H cleaned (at sample temperature 250 °C) surface, which is free from both Sb oxide and Ga oxide, was exposed to ambient air for eight days and reinserted in the UHV chamber for XPS measurement. We found that the Sb oxide, Ga oxide, and C signals reappeared, indicating that an ECR-H cleaned GaSb surface does not resist air oxidation. In fact, previous studies have shown that a bare GaSb surface oxidizes faster than that of GaAs and GaP.[21] Thus, for device applications, an overlayer coating is necessary. One approach to forming an impermiable overcoat is to use a thin nitride layer; such a layer may be formed by exposure to ECR-generated nitro-

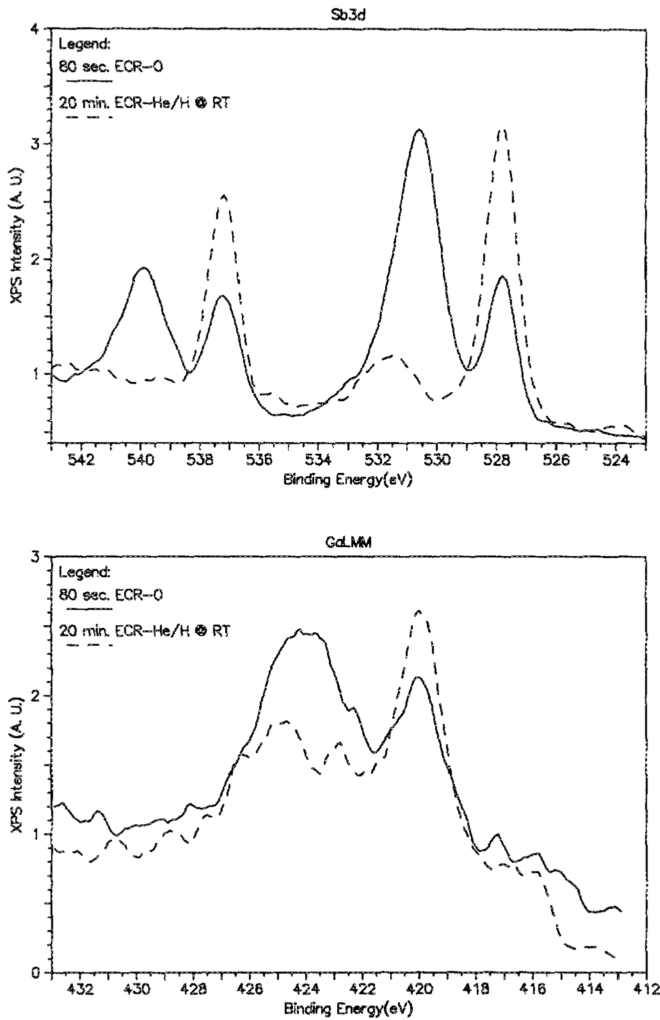

FIG. 4. GaSb surface exposed to an ECR-H_2/He plasma. XPS spectra for Sb $3d$; Ga *LMM* features.

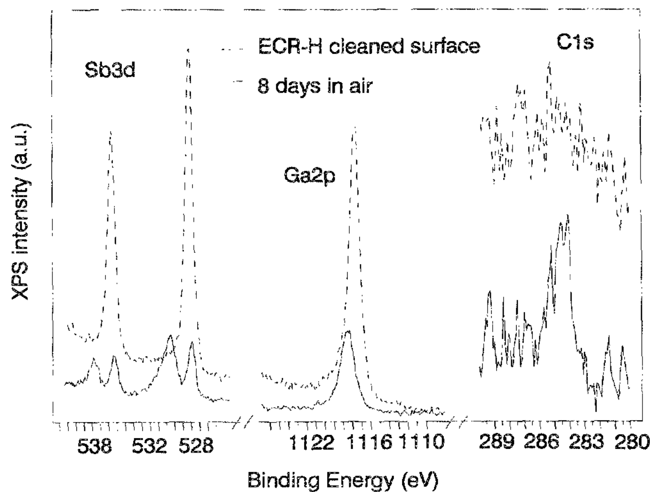

FIG. 5. XPS spectra of the Sb $3d$, Ga $2p_{3/2}$, and C $1s$ core levels for a clean GaSb surface before and after exposing to air for eight days.

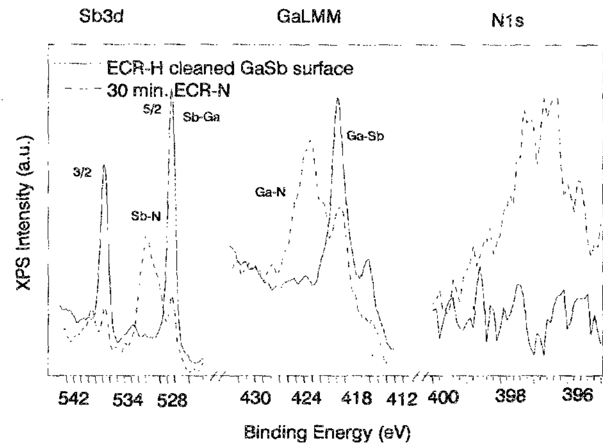

FIG. 6. XPS spectra of the Sb $3d$, Ga *LMM*, and N $1s$ features for a clean GaSb surface before and after exposing to an ECR-N plasma for 30 min.

gen atoms. Figure 6 shows such a previously cleaned GaSb surface after it has been exposed to N atoms from an ECR-nitrogen plasma for 30 min. From the N $1s$, Sb $3d$, and the Ga-$L_3M_{4,5}M_{4,5}$ Auger features, it is seen that a GaSb-nitride layer is formed by the plasma process.

In recent years, electronic and optoelectronic devices based on GaSb have attracted great interest because of their unique device performance and the ability to readily grow $Al_xGa_{1-x}Sb$ layers lattice-matched to GaSb substrates. In particular, AlGaSb avalanche photodiodes (APDs) are now the subject of extensive research and have been shown to achieve lower noise figures and higher gain-bandwidth products than InGaAsP/InP APDs because of the large hole impact-ionization coefficient in AlGaSb.[25] However, without surface treatment, these photodiodes suffer severely from surface-leakage currents, which may overwhelm the signal currents and reduce the signal-to-noise ratios. In order to determine the suitability of our technique for an actual application, we have examined ECR plasma treatment of an AlGaSb PIN photodiode, in which the molecular-beam epitaxially (MBE) grown ma-

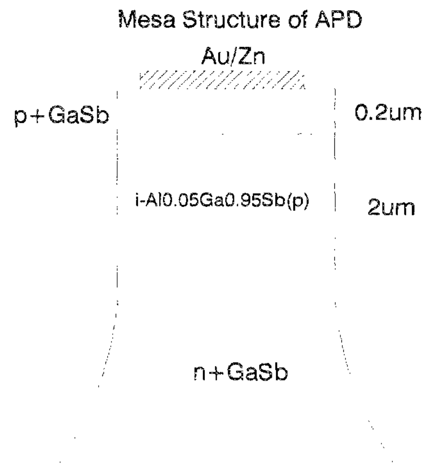

FIG. 7. Mesa structure of a PIN photodiode.

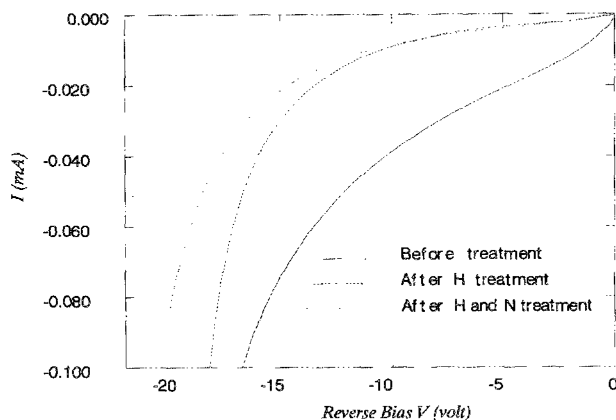

FIG. 8. Reverse I–V curve of a PIN photodetector.

terial is unintentionally p doped. The photodiode structure is schematically shown in Fig. 7. Our electrical measurements (Fig. 8) show that the leakage current after the surface Sb-oxide removal is significantly reduced from that before the ECR-H treatment. With no further treatment, the leakage current of the diode increases again after several days' exposure to the air, undoubtably as a result of regrowth of the native oxide. In order to suppress this Sb-oxide regrowth after ECR-H treatment, we have experimented with ECR-N plasma passivation. XPS measurements on the processed surface show that Ga and Sb nitride are formed on the surface. With the nitride layer in place, the leakage current of a PIN diode remains virtually at the same low values after subsequent atmospheric ambient exposure. In addition, we have observed that all the diodes so processed in the batch showed a consistently similar improvement.

The reduction of diode leakage current indicates that ECR-H plasma either removed a surface conductive path (such as that formed by adsorbed Sb oxide and hydrocarbons), or reduced the surface recombination velocity significantly, or both. For the photodiode shown in Fig. 7, the conductive leakage path could have originated from the very thin, loosely structured oxide from the sidewall of the diode. In this connection, notice that it is only necessary to expose a diode at room temperature to H atoms to remove any possible diode leakage current path originating from the Sb-oxide or airborne hydrocarbon sources. XPS data indicate that a room-temperature H-atom exposure removes Sb oxide and C. Another related observation made separately is that a freshly etched diode has much reduced leakage current in comparison to a diode exposed to air. In this case the treatment removes the surface oxide. Note, it is well known that oxygen exposure to a vacuum-cleaved GaSb surface results in the generation of a high density of surface states.[26] The removal of oxide and carbon would reduce the density of recombination centers significantly, hence reducing the leakage current of the diode. Our XPS data do not clearly allow band bending changes to be monitored by core-level shifts, because of the relatively small band gap of GaSb. We point out, however, that surface hydrogenation is generally effective in passivating the semiconductor interfaces. In fact, a recent photoluminescence study showed that hydrogen efficiently passivated nonradiative recombination centers in GaSb.[27]

Finally, ECR-H treatment has no difficulty in accessing the device sidewalls during cleaning and passivation, whereas other techniques such as overlayer doping or growth,[28] are more problematical. In addition, in the photodiode example, this technique has the additional advantage of avoiding one additional step of pattern definition.

IV. CONCLUSION

We have shown that ECR-hydrogen and nitrogen plasma treatment of GaSb surfaces are effective in removing the carbon and GaSb oxides, and exposure to a subsequent N-atom source forms a protective nitride layer, passivating the surface. We have used the technique to obtain significant reduction of leakage current in a photodiode.

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