Plasma passivation of gallium arsenide*

J. S. Herman and F. L. Terry, Jr.
Center for High Frequency Microelectronics, Electrical Engineering and Computer Science Department, University of Michigan, Ann Arbor, Michigan 48109-2122

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Improved electrical properties of the SiO_2–GaAs interface have been obtained using *in situ* plasma surface treatments prior to film deposition. We present a comparison of several hydrogen based plasma passivation schemes: H_2, H_2/N_2, and H_2S. Hydrogen plasmas remove native oxides, while nitrogen or sulfur form passivating surface layers. Samples were characterized using metal–insulator–semiconductor *C–V* analysis, x-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry. The H_2/N_2 and H_2S treated samples display improved *C–V* characteristics. XPS indicates the presence of nitrogen and sulfur respectively on the uncapped samples, although little evidence remains after SiO_2 deposition. H_2S plasmas offer the best results, providing a self-terminating process that prevents roughening of the GaAs surface by hydrogen plasma etching. However, surfaec doping effects were observed after exposure to high temperatures.

I. INTRODUCTION

The high density of surface states at the dielectric–GaAs interface results in Fermi level pinning[1] that inhibits device performance.[2,3] A well passivated surface with a low interface state density is desirable in the development of a viable metal–insulator–semiconductor (MIS) technology, as well as for the passivation of other III–V devices, such as heterojunction bipolar transistors (HBT).

There are several approaches to improving the electrical properties of the GaAs surface. One method uses aqueous sulfur solutions to coat the wafer surface with a passivating film. These were originally applied using a spin-on Na_2S solution,[4,5] but $(NH_4)_2S$ applied through immersion has shown better performance by being more durable and exhibiting less leakage current in *pn* diodes.[6–8] While there have been remarkable improvements in surface recombination velocity[5] and HBT performance,[4,9] there have been some problems as well, such as poor reproducibility and aging.

A different approach is to use plasma pretreatments prior to dielectric deposition. Hydrogen plasmas are effective in removing GaAs native oxides, but they can also roughen the underlying surface.[10] Photoluminescence (PL) analysis has shown that hydrogen plasmas are effective in reducing the surface recombination and increasing the PL intensity.[11,12] An effective technique incorporates a hydrogen plasma followed by a nitrogen plasma to form a passivating wide band gap nitride layer.[13] H_2/N_2 multipolar plasmas[14] as well as rf discharges[15] have been used to improve the electrical properties of GaAs surfaces.

We recently reported a technique involving a room temperature H_2S plasma followed by a higher temperature (300 °C) plasma enhanced chemical vapor deposition (PECVD) SiO_2 film.[16] This resulted in improved electrical behavior of the SiO_2–GaAs interface, as measured by *C–V* and photoluminescence. In this paper we compare various hydrogen based plasma surface treatments in conjunction with a PECVD SiO_2 film to examine the improvements that can be obtained in the SiO_2–GaAs interface. Hydrogen was either used alone in a H_2 plasma, combined with nitrogen in a H_2/N_2 sequence, or combined with sulfur in a H_2S plasma.

II. EXPERIMENTAL PROCEDURE

The plasma treatments, including the SiO_2 deposition, were performed sequentially in a parallel plate SEMI group model MPB 1000 PECVD reactor operating at 13.56 MHz. Thus there was no air exposure between the plasma pretreatment and the SiO_2 film deposition. The H_2S plasma treatments (200 mTorr, 20 sccm, 80 W), (sccm denotes cubic centimeter per minute at STP) were conducted at room temperature, after which the sample was heated under an argon ambient to 300 °C for SiO_2 film deposition. For the other plasma pretreatments, H_2 (500 mTorr, 30 sccm, 80 W) and H_2/N_2 (N_2 at 100 mTorr, 20 sccm, 80 W), the sample was first heated under an argon ambient to 300 °C, then the pretreatment and film deposition were performed sequentially. The SiO_2 films were deposited from silane, N_2O, and helium at 400 mTorr using 30 W of rf power. The reactor was cleaned with a CF_4/O_2 plasma between runs. Four samples were investigated as follows:

(A) control sample, SiO_2 on GaAs;
(B) GaAs treated with an H_2 plasma, capped with SiO_2;
(C) GaAs treated with an H_2 plasma, then an N_2 plasma, capped with SiO_2;
(D) GaAs treated with a room temperature H_2S plasma, capped with SiO_2.

Samples for *C–V* testing were commerically available metalorganic chemical vapor deposition (MOCVD) grown *n*-type (100) GaAs epitaxial layers 2 μm thick doped to 1×10^{15} cm^{-3} on n^+ substrates. Fabrication consisted of depositing 1000 Å of SiO_2 onto the various samples, evaporating a Ni/Ge/Au ohmic contact onto the back, and then patterning the front with aluminum

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squares. Both metallization steps were done in an electron beam evaporator. The finished samples were annealed in forming gas for 1 h at 300 °C to reduce metallization induced damage and decrease the interface trap density.

X-ray photoemission spectroscopy (XPS) data was taken on plasma treated substrates using a Perkin-Elmer PHI 5400 ESCA system employing a dual Mg(1253.6 eV)/Al(1486.6 eV) $K\alpha$ x-ray source operating at 300 W and 15 kV. The spectra were deconvolved to remove the x-ray source broadening contribution, smoothed to locate shoulders on the peaks, and fitted with combination Gaussian-Lorentzian functions to identify the peak positions and energy separations. The preceding operations were all performed using Perkin-Elmer software supplied with the system. Measurements were taken of the As 3*d*, Ga 3*d*, O 1*s*, N 1*s*, and S 2*p* peaks, but the S 2*p* peak was difficult to analyze due to the overlap with the Ga 3*s* peak and Ga $L_2M_{45}M_{45}$ Auger peaks.

For each sample, XPS measurements were taken of the plasma treated but uncapped surface, which involved unavoidable air exposure as samples were transferred from the PECVD chamber to the XPS chamber. Depth profiles of the SiO_2 capped plasma treated GaAs surface were taken by alternately measuring and removing thin surface layers with an argon ion sputtering gun. The SiO_2 films on these samples were kept thin (approximately 100 Å) to facilitate interface probing.

Spectroscopic ellipsometry (SE) measurements were taken using a Rudolph Research model S2000 operating at 280 to 800 nm. The system consists of a 75 W xenon lamp–collimator–fixed polarizer–rotating polarizer–sample–fixed analyzer–monochromator arrangement, with the parameters $\tan\psi$ and $\cos\Delta$ derived from Fourier transform extractions of the photomultiplier signal.

Electrochemical *C–V* profiling was done using a Bio-Rad PN4250 Polaron system in which the sample is housed in a cell containing an electrolyte that alternately etches the surface layers and measures the capacitance to determine the doping.

III. RESULTS AND DISCUSSION

A. XPS results (uncapped surfaces)

For sample A, the plain GaAs control wafer, XPS reference scans were taken to determine the spin-orbit splitting and peak positions of the semiconductor and oxide components. The sample was degreased in conventional solvents, then etched in $HCl:H_2O$ (1:1), rinsed in DI water and blown dry in N_2 to stimulate a wafer ready for the PECVD chamber. Surface scans of the As 3*d* and Ga 3*d* peaks can be seen in Fig. 1, indicating the *j–j* spin–orbit splitting of the $\frac{5}{2}$–$\frac{3}{2}$ GaAs bulk components and a native oxide component shifted from the $\frac{5}{2}$ component by 3.4 eV for arsenic and 1.5 eV for gallium. The measured values of the spin–orbit split, 0.7 eV for arsenic and 0.5 eV for gallium, agree well with accepted values.[17–19] The surface layers of the sample were removed in the XPS chamber using an *in situ* argon ion sputtering gun, after which only the bulk components remained. The oxide components vanished along with the O 1*s* signal, and the spin–orbit separations again were 0.7 eV for arsenic and 0.5 eV for gallium.

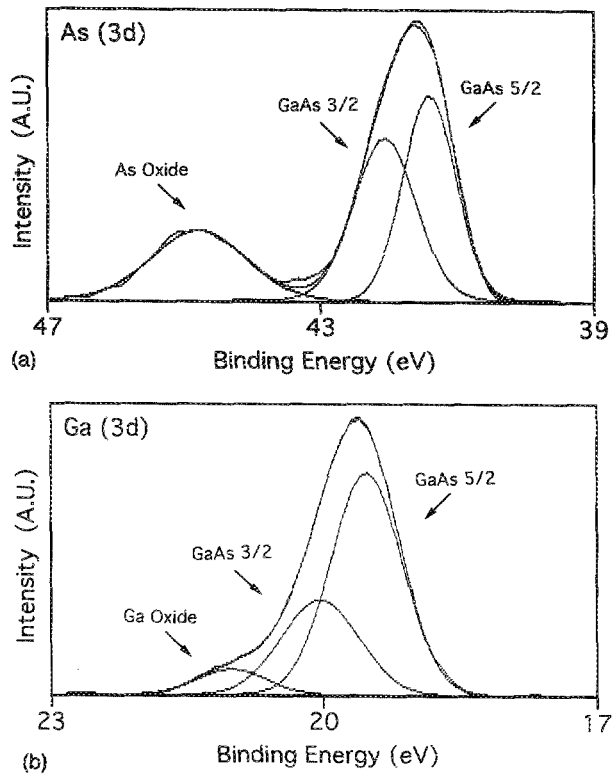

FIG. 1. XPS spectra of the oxidized GaAs surface showing $\frac{5}{2}$–$\frac{3}{2}$ spin–orbit splitting and the oxide component. (a) Arsenic 3*d* peak and (b) gallium 3*d* peak.

To calculate the relative atomic concentrations, the peak intensities are compared using

$$I = \frac{A}{\sigma t}, \tag{1}$$

where I is the normalized peak intensity, A is the peak area, σ is the photoionization cross section,[20] and t is the acquisition time. For the reference sample surface, ignoring the oxide components and examining the underlying $\frac{5}{2}$–$\frac{3}{2}$ bulk components of the Ga 3*d* and As 3*d* peaks yield an As/Ga ratio of 1.0, indicating a stoichiometric crystal under an oxidized surface. For the sputtered reference sample, the As/Ga ratio dropped to 0.6, probably indicating preferential sputtering of arsenic with the argon ion gun.

The gallium and arsenic oxide ratios were calculated using an effective photoionization cross section, since the $\frac{5}{2}$–$\frac{3}{2}$ splitting could not be resolved. The effective cross section was the average of the $\frac{5}{2}$ and $\frac{3}{2}$ cross sections, weighted by the intensities of the bulk signals. The O 1*s* peak consisted of two peaks separated by 1.0 eV, attributed to bonding with either gallium or arsenic. The O_{Ga}/Ga_{ox} ratio is 3.9 and the O_{As}/As_{ox} ratio is 1.9, which is not in agreement with the usual picture of the GaAs native oxide as being a mixture of As_2O_3 and Ga_2O_3. The thickness of the oxide layer was calculated from the uniform layer model[21] where

$$\frac{I_{ox}}{I_{GaAs}} = \frac{d}{\lambda \sin\theta}\frac{n_a}{n_o}\exp\left(\frac{d}{\lambda \sin\theta}\right), \quad (2)$$

where I is the normalized intensity, d is the oxide thickness, λ is the photoelectron inelastic mean free path,[22] θ is the electron takeoff angle, n_a is the adsorbate density, and n_o is the substrate density. This yielded an oxide thickness of approximately 7 Å. A thin room air oxide thus seems to be a nonstoichiometric mixture of oxygen bonded to arsenic and gallium.

To determine operating conditions for the H_2 plasma that would avoid surface roughening of samples B and C, tests were undertaken to determine the minimum exposure time for complete oxide removal. SE was used on thinly capped substrates to identify the presence or absence of native oxides under the SiO_2 film. This was found to be a very abrupt and sensitive etch, with too little time resulting in native oxide left on the surface, and too much time resulting in surface roughening. The point at which complete oxide removal occurred drifted slightly, but that might be due to residual water vapor in the chamber, since the system is not equipped with a high vacuum pump for low base pressure. The H_2 plasmas were run slightly longer than the minimum time determined by SE, to ensure complete oxide removal. Surface analysis of the H_2 plasma treated GaAs sample indicates the presence of gallium oxide but no arsenic oxide. It has been shown that both arsenic and gallium oxides are removed at temperatures above 200 °C,[14] so the gallium oxide probably results from reoxidation as the sample is transferred from the PECVD chamber to the XPS chamber. Figure 2 shows the As 3*d* peak, featuring the usual spin–orbit splitting of 0.7 eV and no indication of the arsenic oxide, as present on the control sample.

Surface analysis of sample C, the H_2/N_2 treated sample, indicates a nitrided surface with a fairly strong N 1*s* peak at 397.7 eV, as well as significant surface oxidation. Figure 2 shows the As 3*d* peak, featuring the usual spin–orbit splitting of 0.7 eV and two additional peaks at 3.8 and 2.1 eV from the $\frac{5}{2}$ bulk component. The component at 3.8 eV indicates the presence of arsenic oxide, with the remaining peak at 2.1 eV attributed to arsenic nitride formation. Although uncommon, plasma growth arsenic nitrides have been observed by other groups.[14,15] Because of the large overlap and small separations of the Ga 3*d* components, analysis is somewhat ambiguous and this peak could be interpreted to have either a large oxide peak or both an oxide and a nitride peak.

Sample D was exposed to a room temperature H_2S plasma, then heated to 300 °C to desorb any excess sulfur and simulate a sulfided wafer ready for film deposition. This sample exhibits much less surface oxygen than any of the other samples, with the presence of sulfur indicating by the S 2*p* peak at 162.2 eV. Figure 2 shows the As 3*d* peak exhibiting the same spin-orbit structure with a separation of 0.7 eV, but having a new peak appear at 2.2 eV from the $\frac{5}{2}$ component, indicating the formation of an arsenic sulfide compound. Interpretation of the Ga 3*d* peak is ambiguous, as it can be fit with two bulk components separated by 0.6 eV and a smaller peak at either 1.5 or 1.3 eV from the $\frac{5}{2}$ component. It is presently not clear if this indicates the presence of a gallium oxide or a sulfide. The sulfide layer is approximately 8 Å thick, as estimated from Eq. (2).

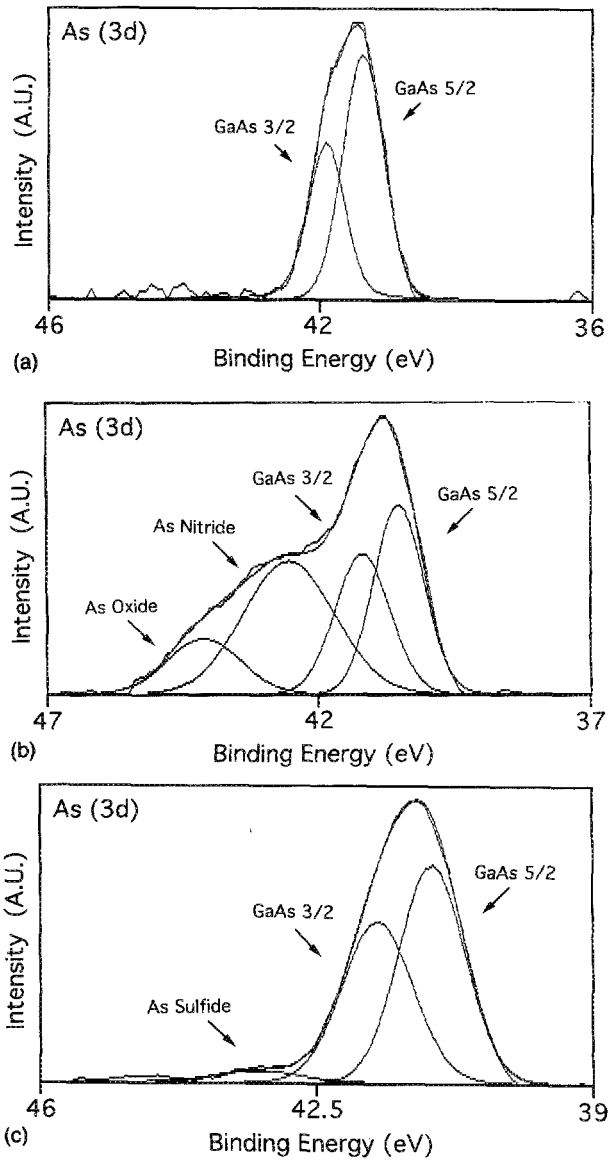

FIG. 2. XPS spectra of the arsenic 3*d* peak after various plasma treatments. (a) H_2 plasma treated GaAs surface showing spin–orbit splitting and no other components; (b) H_2/N_2 plasma treated GaAs surface showing spin–orbit splitting as well as oxide and nitride peaks; and (c) H_2S plasma treated GaAs surface showing the spin–orbit splitting and a sulfide peak.

Surface analysis of the various uncapped plasma treated surfaces indicates an oxidized GaAs surface for the control sample. The H_2 plasma treated surface showed a complete removal of arsenic oxide and the presence of gallium oxide. The H_2/N_2 treated surface shows a distinct nitrogen peak and the definite formation of arsenic nitride, as well as the possible formation of gallium nitride. The H_2S treated surface exhibits very little oxygen, as well as the formation of an arsenic sulfide compound and the possible formation of gallium sulfide. XPS data show that the sulfide terminated surface is more resistant to reoxidation than the H_2/N_2 treated surface.

B. XPS results (depth profiles)

Depth profiles of the SiO_2 capped samples are all remarkably similar in nature. All clearly indicate SiO_2 on top of bulk GaAs with an intermediate transition region. The bulk Ga 3*d* and As 3*d* peaks all show spin–orbit splitting with no shoulders that would indicate oxides, nitrides, or sulfides of any kind. In the interface region, the As 3*d* peaks still exhibit no shoulders, while the Ga 3*d* peaks all now exhibit additional components. However, just as with the surface scans, the large overlap and small separations make it difficult to distinguish between gallium oxides and gallium nitrides or sulfides.

One explanation for the lack of arsenic compounds at the interface is that when heated, arsenic oxides react with bulk GaAs according to the following reaction:[23]

$$As_2O_3 + 2GaAs \rightarrow 4As + Ga_2O_3, \quad (3)$$

thus eliminating the arsenic oxides from the interface. The presence of arsenic oxides on the uncapped surfaces is probably caused by air exposure upon sample transfer.

The N 1*s* peak was also monitored during the depth profiling of sample C. There was no detectable nitrogen at the interface, which is unusual since the H_2/N_2 treated sample showed considerable nitrogen on the uncapped surface. Examination of the S 2*p* peak during depth profiling of sample D indicates the presence of sulfur at the interface, but much less than on the uncapped sample.

A comparison of the surface data with the depth profile data seems to indicate that the initial stages of SiO_2 film deposition eliminate the surface compounds present on the plasma treated but uncapped surfaces. It is possible that an alternate deposition method, such as indirect PECVD (Ref. 24) where the samples are not exposed to the plasma, would preserve the interfacial compounds.

C. *C–V* results

Figure 3 shows the *C–V* characteristics of the control sample and the H_2 treated sample. Both of these are qualitatively similar, exhibiting hysteresis and similar kinks in the plots. The electrical behavior of these samples were dominated by the high trap density present at the interface. Figure 4 shows the *C–V* characteristics of the H_2/N_2 treated sample and the H_2S treated sample. These two are distinctly different from the previous samples, exhibiting steeper, smoother transitions, but still having significant hysteresis. A Terman analysis[25] of the forward curve of both of these samples indicates an interface trap density in the mid to high 10^{11} cm^{-2} eV^{-1} range. A possible explanation for the improved electrical performance is that the nitrogen or sulfur, present on the uncapped surface, forms a sacrificial barrier that prevent reoxidation from the reactive oxygen used for SiO_2 film deposition. Therefore, removal of the native oxides alone is insufficient to improve the electrical properties of the SiO_2–GaAs interface. It is still necessary to form a suitable compound to protect the surface.

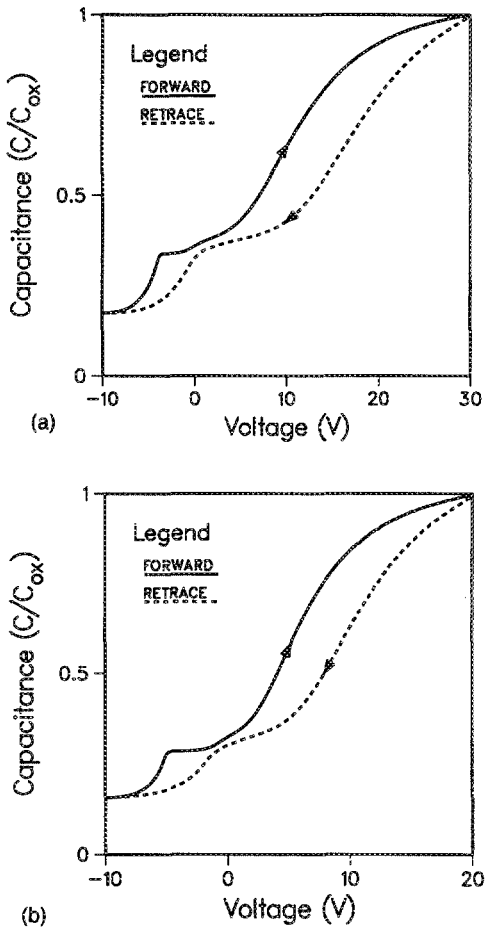

FIG. 3. High frequency *C–V* characteristics of SiO_2 on GaAs. (a) Control sample, no pretreatments, (b) H_2 treated sample.

D. Spectroscopic ellipsometry results

SE spectra were analyzed using existing refractive index versus wavelength data for SiO_2, anodically oxidized GaAs, GaN, and amorphous As_2S_3. Optical data for gallium sulfides and arsenic nitrides were not available. Because of the similarity of the dielectric constants of GaN and GaAs oxides, SE analysis could not resolve whether GaN or GaAs oxides were present at the interfaces of the H_2/N_2 treated samples. The SE spectra show clearly that the interface of the H_2S treated sample is optically different than GaAs oxide; however, use of either a SiO_2/GaAs or a SiO_2/vitreous As_2S_3/GaAs model does not adequately match the experimental data. It is clear from the SE results that the H_2S treated surface remains chemically different from either GaAs oxide or bare GaAs even after SiO_2 deposition; however, it is not known if the interface contains gallium sulfide, off-stoichiometric arsenic sulfides, or elemental S.

E. Electrochemical profiling

Electrochemical profiling was used to test if sulfur, an *n*-type dopant in GaAs, would adversely affect the water wafer surface, especially after high temperature processing. Two pieces of *C–V* material (1×10^{15} cm^{-3} on n^+) were treated with a H_2S plamsa coated with SiO_2. One sample

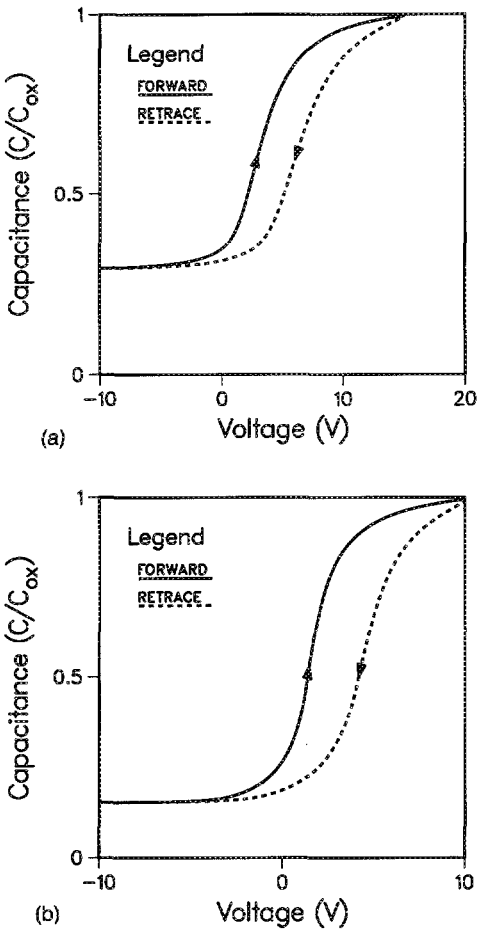

FIG. 4. High frequency C–V characteristics of SiO_2 on GaAs. (a) H_2/N_2 treated sample, and (b) H_2S treated sample.

was heated in a rapid thermal annealer at 950° for 5 s, parameters typically used to activate ion-implanted GaAs. Both samples had their oxides stripped and were probed with the profiler. The unheated sample exhibited the specified value of $(1–2)\times10^{15}$ cm^{-3} all the way to the n^+ substrate, but the heated sample exhibited a surface doping around 5×10^{17} cm^{-3} that decayed over several hundred angstroms to the nominal doping value. Further work is required to determine the implications of this effect for metal–insulator–semiconductor field-effect transistor (MISFET) fabrication.

IV. CONCLUSION

The use of plasma pretreatments has been shown to be effective in improving the electrical properties of the SiO_2–GaAs interface. However, removal of the native oxides alone is not sufficient; the bare semiconductor surface must then be passivated with a suitable compound. A combination H_2/N_2 treatement can be effective, but this requires tight control over the hydrogen plasma parameters to maintain good morphology. H_2S is the most robust plasma pretreatment, since the the formation of arsenic sulfide automatically terminates the hydrogen plasma oxide etch. This not only avoids the possibility of roughening the GaAs surface by over etching, but also provides a stable sruface that resists reoxidation. However, surface doping effects do occur when H_2S treated GaAs is exposed to elevated temperatures.

ACKNOWLEDGMENT

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