

Photoelectrochemical passivation of GaAs surfaces

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A wet chemical technique is described for passivating air-exposed GaAs surfaces. The passivating layer is elemental arsenic which forms as a result of illuminating an *n*-type GaAs wafer immersed in a mixture of HCl acid and deionized 18 M Ω water with light from a mercury vapor lamp at intensities of 0.01–0.05 W·cm⁻². Studies using XPS, LEED, and UPS show that the passivated surfaces have the following properties: (1) there is little or no Ga or Ga and As oxide species in the As film or at the film/GaAs interface; (2) a strong GaAs LEED pattern is observed after a 290 °C anneal following low energy ion beam bombardment. This suggests that the As/GaAs interface formed by photoetching is free of contaminants and that the GaAs surface is well ordered prior to ion bombardment or heat treatment. Thus, clean, well ordered surface of GaAs which have been previously air exposed can now be obtained at lower temperatures than previously. This creates new possibilities for surface studies, epitaxy, and metallization.

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I. INTRODUCTION

In order to form clean, well-ordered surfaces of GaAs for MBE growth, or for surface sensitive studies such as UPS, high temperature (≥ 500 °C) processing is typically required. In the absence of ion bombardment, the requisite temperatures are typically $T \geq 580$ °C. At these elevated temperatures, surface science studies are hampered due to the irreversible effects often observed on cleaved surfaces. Also high temperature cleaning could cause effects, e.g., surface reconstructions, which are incompatible with lower temperature MBE growth studies. Furthermore, elevated temperature baking precludes the use of conventional photoresist patterning to define device structures during MBE growth.

In this paper, we discuss an alternative approach to the preparation of atomically clean, well-ordered GaAs surfaces at substantially lower temperatures. This technique exploits the recent use of an As passivating layer to protect MBE grown GaAs surfaces from ambient effects during prolonged exposure to atmospheric conditions.¹ In contrast to previous work, however, we do not require UHV conditions to prepare the clean GaAs surface prior to As passivation. Rather, we prepare the substrate using standard chemical cleaning procedures, then immerse the *n*-type sample in a 1:1 HCl:H₂O solution for 10–30 min while irradiating the sample with 0.01–0.05 W/cm² of photons of energy > 1.8 eV. After subsequent rinsing and air exposure, the sample is inserted into our vacuum system. Annealing at 150 °C will desorb most of the surface As, and annealing at 300 °C provides a surface showing a strong LEED pattern. XPS studies of the surface prior to these annealing procedures indicate that the photoetching process has left a thin As film on the surface.

II. PREVIOUS WORK

It is well known that when *n*-type GaAs is illuminated with greater than band gap energy light in the presence of either an acid or basic aqueous solution, photodecomposition will occur.^{2,3} The basic theoretical construct invoked to

explain this phenomenon is that the presence of excess carriers at the semiconductor/electrolyte interface will reduce the bond strength of semiconductor atoms or molecules at the interface. This in turn will increase surface chemistry reaction rates, e.g., oxidation. If the reaction products are mainly ions, radicals, or oxides which are highly soluble in acid or base, then the photoetch rate will be proportional at low intensities to the incident photon flux. For *n*-type GaAs immersed in aqueous acid or base the energy band diagram is similar to that for a metal/*n*-GaAs photovoltaic device. Thus, under "short circuit" conditions, the band bending will drive holes to the GaAs/electrolyte interface. The holes being the excess carrier enhance the etch rate. In fact using a 1 M KOH solution, it was found³ that the efficiency of converting impinging 550 nm photons into dissolved GaAs is about 40%, at a light intensity of 2.6 mW·cm⁻². Also, the importance of net excess carriers at the interface on photoetch rate has been demonstrated. Under "open circuit" conditions, where the electron and hole current densities across the interface were made nearly equal, the photoetch rate was reduced by a factor of 4. Thus, without external electrodes, photoetching will only be assured by draining electrons from all surfaces of the samples via injection over the Schottky barrier formed by the GaAs/electrolyte interface. This forces the hole current density to be greater than the electron density at the illuminated surface/electrolyte interface and is also the reason why the electrolyte must be allowed to flow freely across both surfaces in the photoetch apparatus discussed below. Thus, for *n*-type GaAs the use of greater than band gap photons which produce a net hole current across the interface is equivalent to adding peroxide to an aqueous acid or base, i.e., there is no significant etch rate until either is present.

There is a considerable amount of work reported in the literature concerning reaction products on GaAs surfaces when these reaction products are primarily stable oxide species formed by aqueous anodization,^{4,5} plasma anodization,^{6–8} and thermal oxidation.⁹ The observations are nearly

all the same: the films are composed of Ga and As oxides with various amounts of elemental As at the GaAs/oxide interface, depending on the method of formation. These observations are consistent with theoretical predictions based on thermodynamic data.⁹ However, there are only a few recent studies which have unravelled the nature of the reaction products on surface exposed to acids, bases, and etchants. Noteworthy are the studies of Aspnes *et al.*¹⁰⁻¹¹ and Frese and Morrison,¹² who found that elemental As is formed on GaAs when either etched in acids of *pH* less than 2.7 with small concentrations of peroxide, or soaked in HCl (presumably in the dark or low level light). It is a purpose of this paper to describe the nature of the reaction products on GaAs surfaces which have been photoetched.

III. EXPERIMENT

The samples used in this experiment were (100) bulk wafers of *n*-type GaAs doped with Si in the range $1-10 \times 10^{17} \text{ cm}^{-3}$ and polished by the vendor. Prior to the photoetching experiments, the samples were usually cleaned and etched. However, passivating As films were also obtained on as-received wafers. In general, more consistent results were observed on etched wafers. Two types of etched surfaces were studied: (1) 7:1:1-H₂SO₄:H₂O₂:H₂O for 1 min, water quenched and blown dry with nitrogen; (2) 3:1:15-NH₄OH:H₂O₂:H₂O for 1 min and direct transfer to the photoetch solution without either a water quench or a blow dry. (The latter etching procedure was successfully used when the direct transfer was replaced by a water quench and blow dry step.) The photoetch solution was usually 1:1HCl:H₂O. However, this ratio was not critical as As films were obtained for water to acid ratios as high as 10:1. This is consistent with previous observations^{10,13} that metallic As is stable in aqueous solutions with a *pH* of less than 3. More critical, however, is the condition of the water used to form the photoetch solution. It appears that in order to form As films rather than films of Ga and As oxides, it is necessary to use fresh 18 M Ω deionized water. It was found that oxygen contamination of the water prior to the photoetch resulted in films containing Ga and As oxides. This observation is also consistent with the observations of Aspnes *et al.*, who found that postetching films on GaInAs contained more oxide species when the concentration of peroxide in the etchant was increased.^{10,11} The light source for these experiments was a collimated mercury vapor lamp operated at an intensity of 0.01-0.05 W-cm⁻² at the sample position. For this range there was no evidence that the film properties depended on illumination intensity. The photoetching times were 10-30 min. For reasons discussed above, it was found that it is important to place the sample in an etching apparatus which allows the solution to flow freely around both the illuminated and nonilluminated surfaces. A quartz or Teflon beaker with a round bottom will suffice for this purpose.

IV. RESULTS AND DISCUSSION

A. XPS core level spectroscopy

Figure 1 shows typical XPS results for the As 3*d* and Ga 3*d* core levels of an *n*-type sample photoetched in 1:1

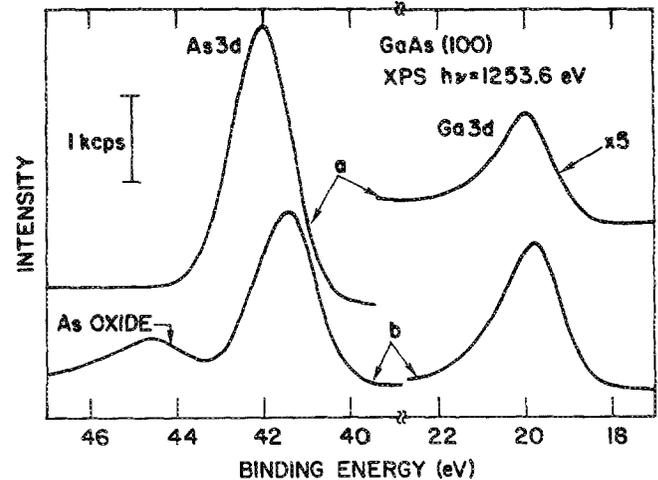


FIG. 1. Ga and As 3*d* core level spectra determined by XPS; (a) photoetched GaAs sample (see the text); (b) GaAs sample prepared by normal etching procedures (see the text). Note that the samples received no *in situ* surface treatment prior to the measurement. It is seen that the photoetched sample has a surface containing much more As than the normal sample. Also, there is no peak related to As oxide in the photoetched sample.

HCl:water for 30 min at a light intensity of about 0.025 W-cm⁻² [Fig. 1(a)]; and an *n*-type sample prepared by the normal etching procedure used for samples for MBE (7:1:1-H₂SO₄:H₂O₂:H₂O plus water quench) [Fig. 1(b)]. The measurements in Fig. 1 were made on the as-prepared samples after pump down in UHV conditions.¹⁴ Figure 1(a) clearly demonstrates that photoetching leaves a film that is As rich at the surface. From the data in Fig. 1(b) and from data taken on other MBE grown samples, the peak area ratio of Ga to As is approximately 0.7 which is the value of a stoichiometric surface, i.e., Ga atom fraction = As atom fraction. From Fig. 1(a), the corresponding ratio for the photoetched surface is 0.07. The mean escape depth of photoelectrons with energies of about 1200 eV is approximately 2 nm. If it is assumed that the film is a uniform layer of As, calculations indicate the thickness to be 5 nm.

In addition, the XPS spectra of Fig. 1 show the relatively low oxide content of the photoetched sample compared with the normally etched sample. Whereas the latter sample [Fig. 1(b)] shows a distinct As oxide peak (at a binding energy of 44.6 eV) the photoetched is almost free from As oxide by XPS standards. A comparison of the O 1*s* core level intensities (not shown in Fig. 1) of the two samples shows that the oxygen content of the photoetched sample is about 20% of the amount in the normally etched sample.

B. UV photoelectron spectroscopy and LEED

A photoetched sample similar to the one of Fig. 1(a) was precleaned by a combination of low energy ion bombardment (150 eV Ar⁺) and heat treatment (145 °C) in order to remove surface contaminants. This treatment reduced the thickness of the As film from about 5 to about 3 nm. The UPS spectrum of this "cleaned" As film is shown in Fig. 2. Note that for UPS conditions the escape depth of the photoelectrons is now about 0.5-1 nm, and therefore, the spectrum should not be influenced by the GaAs substrate. The UPS

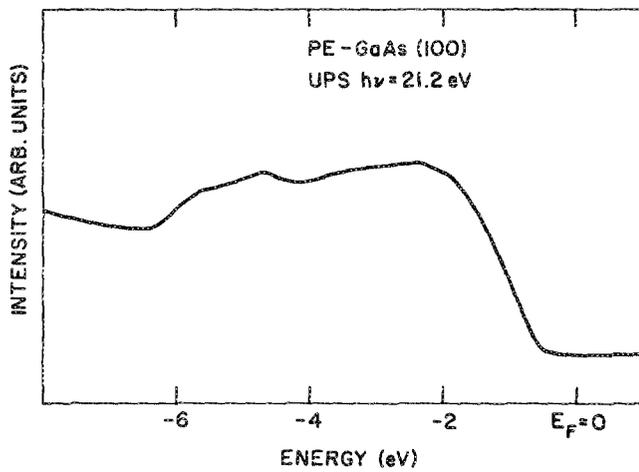


FIG. 2. Normal emission UPS spectrum of the As film on the photoetched sample after 150 eV/145 °C-ion bombardment/heat treatment to remove surface contaminants. Note that the Fermi level E_F is well above the valence band edge indicating a semiconducting phase of As.

spectrum of Fig. 2 clearly shows the As is *not in a metallic phase*, since the Fermi level E_F is located well above (0.5 eV) the valence band edge, and hence, the As film is in a semiconducting state, possibly amorphous As.¹⁵

Figure 3 shows the UPS spectra of: (a), a normally etched sample heat cleaned at 600 °C (the procedure normally used for MBE substrates) and (b), a photoetched sample cleaned by a combined low energy ion beam bombardment and heat treatment (150 eV/290 °C). A comparison of Figs. 3(a) and 3(b) shows that the surface quality of the photoetched sample cleaned at 290 °C is at least as good as if not better than the

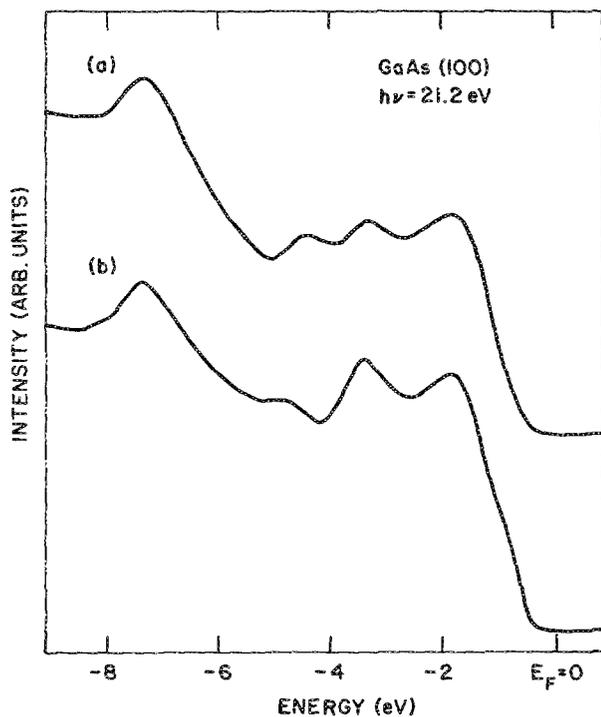
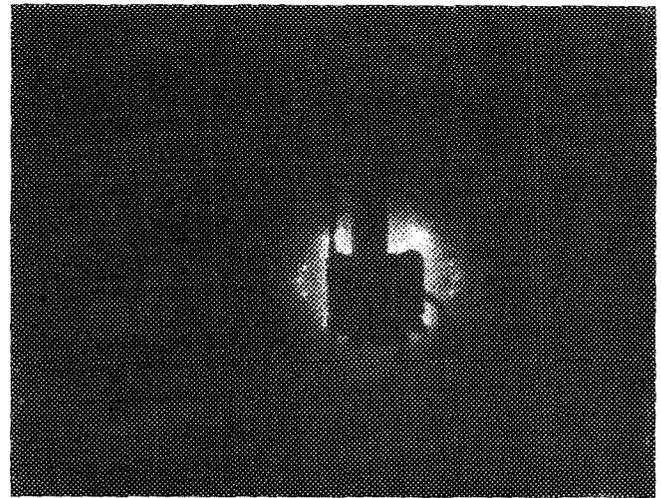


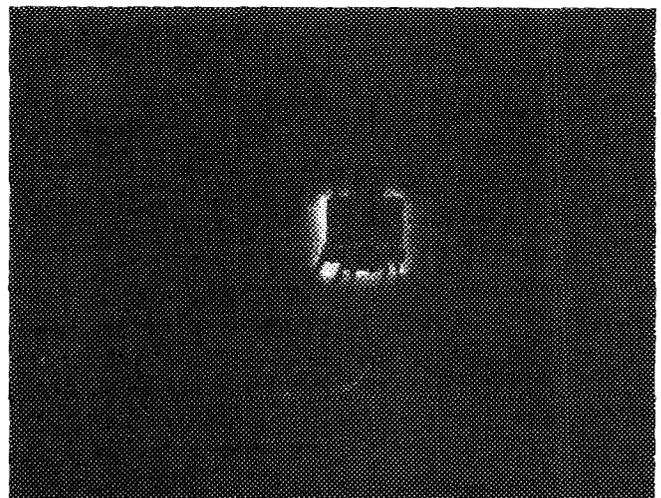
FIG. 3. UPS spectra of: (a) GaAs sample normal etch/heat clean-600 °C (b) photoetched GaAs sample (150 eV/290 °C)-ion bombardment/heat treatment. The spectra have been measured at normal emission and at an angle of 45° for the incident light.

sample prepared by normal etching and heat treatment at 600 °C. In this context the "quality" of the surface is judged by the relative intensity of the different peaks in the valence band spectra of Fig. 3, and the relative amount of scattered electrons which, in general, increases less with decreasing energy, for more perfect surfaces.

A LEED pattern of the photoetched sample of Fig. 3(b) is shown in Fig. 4(a). In contrast to a sample prepared like the one in Fig. 3(a) [Fig. 4(b)], the LEED spots of the photoetched sample are sharp and exhibit a relatively low background. Thus, from a structural and contamination point of view, a surface prepared by the procedure of photoetching, low energy ion bombardment/heat treatment (150 eV/290 °C), is superior to that prepared by the procedures normally used to prepare samples for MBE growth. Furthermore, this better surface is obtained at temperatures compa-



(a)



(b)

FIG. 4. LEED patterns of: (a) GaAs sample normal etch/heat clean-600 °C, beam energy = 120 eV; (b) photoetched GaAs sample (150 eV/290 °C)-ion bombardment/heat treatment, beam energy = 117 eV.

tible with those used with current semiconductor lithography and metallization techniques, and thus allows new possibilities for GaAs device processing.

Several samples prepared by photoetching for different times and using different light filters have been analyzed. The results are qualitatively the same as those discussed above. However, there are some notable quantitative differences. For example, the XPS values of the Ga/As ratio can vary from 0.06 to 0.53. This has, so far, correlated with etch time but not with photon energy, i.e., longer etch times result in lower Ga/As ratios. Also, different cleaning procedures have been studied including combinations of low energy ion bombardment and heat treatment. For example, LEED patterns have been observed even after a cleaning procedure of a 200 eV Ar⁺ ion bombardment followed by a 160 °C heat treatment. However, the quality of the surface could be improved by increasing the annealing temperature, typically up to 290 °C.

Finally, of all the parameters studied thus far, the conditions of the water seems to have the greatest affect on the nature of the films which result from photoetching. Films generated by photoetching in solutions of HCl and water saturated with oxygen contain primarily Ga and As oxides and carbon, rather than just As, as determined by XPS. This is not very surprising in view of the results of Aspnes and Stocker^{10,11} who showed that the presence of peroxide in aqueous acid solutions generated films with oxide components. Thus, these preliminary results suggest that in order to reproducibly form As films by photoetching it is necessary to use freshly prepared solutions of oxygen-free HCl and 18 M Ω deionized water.

V. CONCLUSIONS

It has been shown that when air-exposed *n*-type GaAs wafers are photoetched in solutions of HCl and water care-

fully purged of oxygen, films of elemental As are produced which are about 5 nm thick. These films can be removed in UHV conditions by a combination of low energy ion bombardment and low temperature heat treatment (150 eV/290 °C) leaving a surface which is more perfect than that produced by MBE procedures, e.g., heat treatment at 600 °C. This suggests that the As/GaAs interface formed by photoetching is free of contaminants and that the GaAs surface is well ordered prior to ion bombardment or heat treatment. This may allow new possibilities for GaAs device fabrication.

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