SURFACE CHEMISTRY OF GaAs(100) AFTER TREATMENT WITH AQUEOUS H_3PO_4 SOLUTION

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ABSTRACT

The interaction of semiconductor surfaces with aqueous acid solutions is important in chemical cleaning and etching. Wet chemical treatments are advantageous because they cause little damage to the surface and do not usually require high temperatures. The surface chemistry of GaAs after treatment with phosphoric acid was studied using multiple internal reflection infrared spectroscopy. The treatment left behind a thin film containing several types of P_xO_y bonds. The chemical nature of the film was observed to change with time as new species would form on the surface.

INTRODUCTION

Although gas-phase methods are replacing liquid based processes for cleaning and etching of semiconductors, liquid based methods still enjoy extensive use in stripping and cleaning operations. Ideally, any surface chemical process would remove only undesired material, and leave behind a surface chemically and morphologically compatible with subsequent processing steps and which has the desired electronic properties. Though some nearly ideal liquid-based processes exist for cleaning of silicon, processes for GaAs are much less well-developed. In addition, most liquid based methods have been developed with little knowledge of the underlying chemistry. As a result, the success of such processing is unpredictable, and dependent upon apparently obscure details of the process recipe. For example, treatment of GaAs with buffered hydrofluoric acid has been shown [1] to leave behind a residue of ammonium fluorides which reacts with the surface to form ammonium hexafluorometallates if the treatment is not followed by an immediate thorough water rinse.

Surface infrared spectroscopy is a low energy photonic technique which has been implemented in numerous studies, primarily for investigating adsorption and reaction at metal surfaces but has been finding increased use as a probe for semiconductor surface chemistry. In this study GaAs(100) was treated with 50% H_3PO_4 solution and a time dependent surface infrared study was performed.

EXPERIMENTAL DETAILS

Surface infrared spectroscopy in the multiple internal reflection mode was used to investigate the surface chemistry of GaAs after treatment with

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aqueous phosphoric acid solution. The semi-insulating (100)- oriented GaAs sample was polished on both faces and cut to 4 cm x 2 cm x 0.5 mm. The 2 cm edges were beveled to 45° in the form of a parallelogram prism. Modulated infrared light supplied by a Nicolet 60SX FTIR spectrometer was focused onto one beveled edge. It entered into the sample, reflected multiple times from the sample faces, exited from the other beveled edge, and was focused onto a liquid nitrogen-cooled HgCdTe detector. Each spectrum was signal averaged from 1024 interferogram scans.

The GaAs sample was first cleaned/degreased successively in methanol and deionized water before it was mounted in the sample cell. After the sample was aligned, the beam path was purged and the background spectrum was collected under the nitrogen purge. Chemical treatments were performed in room air, using stock reagents of deionized water and phosphoric acid solution (50 % by weight). The sample was treated by immersion in the phosphoric acid solution for approximately 90 seconds, then withdrawn from the solution and mounted in the optical bench. Approximately 6 minutes elapsed between removal of the sample from the solution and the initiation of data collection. Several signal-averaged spectra were collected at regular time intervals for more than 48 h following treatment. The optical path, including the sample, was kept under continuous dry nitrogen purge to minimize infrared absorption by atmospheric CO_2 and water. This purge also served to limit the exposure of the sample to water vapor and oxygen.

RESULTS AND DISCUSSION

Figure 1 shows the spectrum of the GaAs surface immediately after removal from H_3PO_4 solution (without rinsing) ratioed to the spectrum of the sample collected before treatment. A large negative peak appears at 770 cm^{-1}, indicating that native oxide on the GaAs was removed. The large complex of bands in the region from 700 - 1300 cm^{-1} occurs in the region where most P_xO_y absorptions would be expected. Nakamoto [2] lists typical frequency ranges as 300 - 650 cm^{-1} for O-P-O bending; 900 - 1200 cm^{-1} for P-O stretching; and 1200 - 1500 cm^{-1} for P=O stretching. This spectrum shows clear peaks at 830, 880, 940, and 1130 cm^{-1}. Though we have not as yet definitively identified the species present in this film, we can assert with some confidence that the species do *not* likely include hypophosphite (due to the absence of sharp peaks in the 800 - 850 cm^{-1} region), metaphosphate (due to the absence of a strong peak near 1300 cm^{-1}), and not pyrophosphate (sue to the absence of a very strong peak near 1100 - 1200 cm^{-1}. Based on the assignments of Stegner [3], the peaks likely result from the presence of orthophosphate species, as evidenced by the very strong absorption at 940 cm^{-1} (symmetric stretch of the PO_4^{3-} ion). The associated cations of the phosphate in the film likely include H^+ and Ga^{3+}. Gallium orthophosphate ($GaPO_4$) is especially favored, having a formation free energy of -301 kcal/mol [4]

Figure 2 shows differential spectra of the treated surface 24 and 48 hours after treatment, ratioed to the spectrum collected immediately after treatment. In this manner, small changes which occur on the surface as a function of time are more easily discerned in the spectra. This figure shows

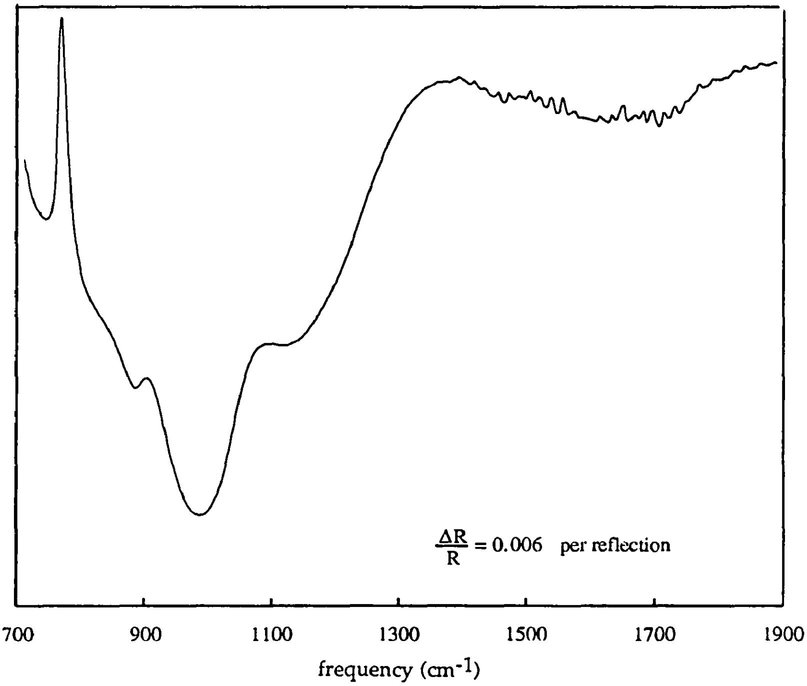

Figure 1: Infrared spectrum of GaAs surface after treatment with H_3PO_4, ratioed to the spectrum of clean GaAs.

some rather surprising features. First, it can be seen that the amount of infrared-absorbing material on the surface is *increasing* with time. A new peak has appeared at 1440 cm^{-1}. The peaks identified at 830, 880, 940, and 1130 cm^{-1} all show an increase at 24 hours, and a further increase at 48 hours after the sample was removed from the H_3PO_4. Further, it can be seen that these peaks do not all grow in at the same rate, suggesting that the species exhibiting these absorptions form at different rates. This is analogous to the behavior of GaAs upon treatment (without rinsing) with NH_4F/HF solution [1], where several different fluoride salts will slowly react and form on the surface over several days following treatment. The most surprising difference from the NH_4F/HF case is that here there is no infrared evidence of species being *consumed* on the surface. The species which are forming on the surface must then be forming by the reaction of species which are not infrared-active in the frequency region covered. Though the nitrogen environment of the sample after treatment limits the sample's exposure to oxygen, it is quite likely that the species which are forming, do so from the reaction of sub-oxidized P on the surface with gaseous oxygen. All of the species P_2O_5, H_3PO_2, and H_3PO_3 are hygroscopic, eventually tending to form H_3PO_4 [5], or in contact with the Ga in the substrate, we would expect the formation of $GaPO_4$.

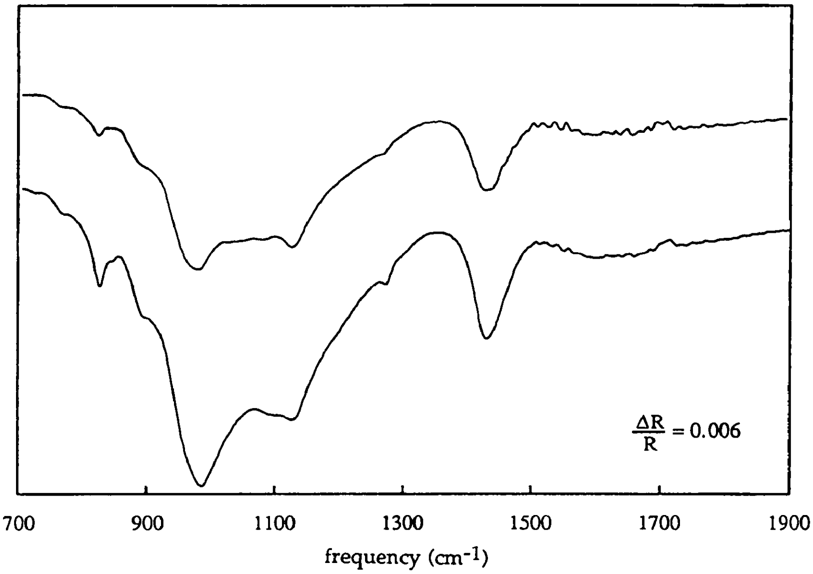

Figure 2: Differential time dependent changes in the infrared spectrum of the GaAs surface after treatment with H_3PO_4; a) 24 hours after treatment ratioed to immediately after treatment; b) 48 hours after treatment ratioed to immediately after treatment.

Under normal conditions, samples treated in liquid reagents are thoroughly rinsed after treatment. For this system, thorough rinsing would remove the residual film left by the phosphoric acid, as well as prevent the slow surface reactions. It is not always possible, however, to assure thorough rinsing of all surfaces of a wafer. For example, any small features existing on the surface, such as trenches or vias, would tend to retain liquid solutions, due to surface tension. In addition, water rinsing often has enough undesirable effects itself (oxidation, photooxidation, and preferential oxidation/dissolution of one component), that rinsing might be avoided in a particular process. In such cases, reactions of the type measured here could be significant.

CONCLUSIONS

The surface chemistry of GaAs after treatment with phosphoric acid treatment has been investigated using surface infrared reflection spectroscopy. The treatment left behind a thin film on the surface which changed in chemical nature with time. The presence of such films after treatment, if undetected could lead to the presence of an unstable residual film, with potentially undesirable physical, chemical and electrical properties. Thorough water rinsing of GaAs after liquid treatment is essential in preventing the deposition and formation of such films.

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