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CHARACTERISTICS OF OXIDE LAYER GROWN ON GALLIUM ARSENIDE USING 2.8 eV TRANSLATIONAL ENERGY ATOMIC OXYGEN

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ABSTRACT

Thick (>200 Å), uniform, oxide layers have been produced on GaAs (110) and (100) by reacting the substrate ($T_s < 160$ °C) with high translational energy (1-3 eV) neutral atomic oxygen at flux levels of ≈ 100 monolayers/second. The Ga and As species are formed in their highest oxidation states respectively which implies formation of either Ga_2O_3 and As_2O_5 or GaAsO_4 . Raman spectroscopy indicates that there is no metallic (amorphous or crystalline) As in the oxide or at the interface between the oxide and substrate and that there is no appreciable oxidation induced disorder of the substrate as is seen in high temperature thermal oxidation processes.

INTRODUCTION

The inherent theoretical advantages of GaAs electronic devices over those employing Si technology are severely limited in practice by the difficulty of forming passivating oxide layers[1]. Problems encountered with oxide stoichiometry, crystallinity, interface defects, and chemical stability have been the subjects of numerous studies over the last 15 years[2-8]. One of the major factors contributing to these problems is the differing rates of oxidation of Ga and As and the volatility of the As_2O_3 and As_2O_5 products at temperatures above ~ 100 °C.

A number of different approaches to the growth of device-quality native oxides at low temperatures on GaAs have been attempted including: the use of ozone[2]; simultaneous O_2 and electron beam exposure[3]; photoexcitation of electron-hole pairs in the GaAs[4, 5]; the use of more reactive oxidizers[4,6] such as N_2O ; photochemical excitation of the gas-phase molecular species[6]; addition of H_2O to the O_2 [7]; excitation of O_2 with a hot filament[3] or a Tesla discharge[7]; and plasma excitation[8] of the O_2 . Although, many of these techniques can greatly increase the rate of formation of the first few monolayers of oxide, they are generally unsuccessful in the growth of >100 Å thick oxide layers. Further, the oxidation reactions do not result in Ga or As in their highest formal oxidation state, and the resulting oxide is usually deficient in Ga or As.

RESULTS

The oxidation of GaAs with a high kinetic energy beam of atomic oxygen has been investigated using x-ray photoemission (XPS) and Raman spectroscopies to characterize the thickness and stoichiometry of the oxide and to probe the oxide/GaAs interface. The energetic atomic O beam source is based on a laser sustained discharge[9] is shown in Figure 1. The

Figure 1. Continuous optical discharge plasma atomic oxygen beam source. A 1500 watt cw CO₂ laser is focused to produce power density of $\sim 10^9$ watts/cm² and a plasma temperature of 12-15,000 K. An isentropic expansion produces neutral atomic oxygen beam kinetic energies ranging between 1-3 eV.

output of a cw 1500 watt CO₂ laser is focused in the throat of a hydrodynamic expansion nozzle creating a plasma having a temperature of 12000 K to 15000 K. The isentropic expansion produces a 2.8 eV O-atom beam (FWHM of ~ 1.0 eV) with a flux of $\sim 5 \times 10^{16}$ atoms/cm²-sec (i.e. ~ 50 monolayers/sec). The GaAs samples were (110)- or (100)-oriented wafers that were either Si-doped ($\sim 2 \times 10^{18}$ /cm³) n-type or semi-insulating and were repolished in a freshly prepared 1% Br₂/methanol solution prior to use. The samples were exposed to the atomic O beam over an area of about 5x7 mm at a distance of 15 cm from the source for periods of up to 5 hours, during which time the sample temperature was held constant. Following atomic O exposure, the samples were transferred in air to an ultra-high vacuum chamber for XPS analysis using Al K α excitation ($h\nu = 1487$ eV). Ar⁺-ion sputter profiling was done using a 4.5 keV, 6 μ A/cm² beam at a sputter rate of ~ 50 Å/min. Raman spectra were obtained in air using the 488 nm line of an Ar-ion laser and a triple monochromator with a cooled optical multichannel analyzer (OMA) detector array in a backscattering geometry with either s- or p-polarization of the incident beam and no intentional polarization of the scattered beam.

A representative example of the Ga and As 3d core-level XPS data obtained at two distinct locations on an atomic O exposed sample held at 50 °C during oxidation are shown in Figure. 2. The As 3d binding energy (BE) shift, relative to that of the unexposed GaAs area, is about 3.2 eV near the edge of the O-exposed area and about 4.2 eV at the center. Reference to standard compounds[10,11] shows that a 3.2 eV BE shift corresponds to As₂O₃ (3.2-3.4 eV), while a shift of 4.2 eV is approaching that of As₂O₅ (4.7-4.9 eV). Oxidation-induced BE shifts are generally smaller[11,12] for Ga than for As 3d. At the center of the O-exposed area, the Ga 3d BE shift of 1.0 eV corresponds to that of Ga₂O₃ (0.9-1.4 eV), while the smaller shift near the exposed area indicates that the Ga is less than fully oxidized. It is worth noting that there is no sign of the "parent" (i.e., unoxidized) Ga or As 3d peaks at the center of the O-irradiated area. The attenuation length for 1400 eV photoelectrons in GaAs is estimated[12] to be about 27 Å giving an effective sampling depth for the spectra in Figure. 1 of ~ 50 Å. Therefore we conclude that the substrate is completely reacted to at least the depth sampled.

Figure 2. Ga and As 3d core-level XPS (Al $K\alpha$ excitation) for two regions of the GaAs(110) surface exposed to atomic oxygen at a substrate temperature of 50 °C. The dashed line is at the edge of the exposed area and solid line is at the center of the exposed area.

The oxidation rate at a substrate temperature of 50°C was investigated by exposing 3 separate spots on the same GaAs (100) wafer in sequence having different exposure times. XPS analysis of these samples are shown in Figure 3 with exposure times of 0.5, 1, and 3 hours representing total atomic oxygen doses of 9×10^4 L, 1.8×10^5 L, and 5.4×10^5 L.

Figure 3. Time dependence of oxidation state of GaAs (100) at a substrate temperature of 50 °C. Exposures were made sequentially for 0.5 hr, 1.0 hr, and 3.0 hr without altering the atomic oxygen beam intensity and only changing the sample position.

position.

respectively. Increasing exposure time results in increased oxidation state and a continual decrease in intensity of the metallic arsenic line at BE of 41 eV. All other samples whose analysis is presented in this paper were exposed for 5 hours independent of substrate temperature.

Ar⁺-ion sputter profiling and XPS analysis were performed to evaluate the thickness and composition of the oxide layer. The raw data were converted to atomic percent and show an apparent excess of Ga at long sputter times in agreement with the observed preferential sputtering of As reported for oxide-free GaAs surfaces[13]. However at short sputter times the Ga/As atomic ratio is similar to that of virgin GaAs and shows only a small variation as sputtering progresses through the oxide and into the substrate, and there is no observed excess of either Ga or As at the oxide/substrate interface. The As 3d oxide satellite shows only a slight BE shift (from 4.2 to 4.0 eV) as profiling progressed through the oxide and the "parent" As peak gained intensity. These results indicate that the oxide layer has a nearly uniform chemical composition. We tentatively conclude that the oxide layer is GaAsO₄ (gallium arsenate) but note that the BE shifts[11] for GaAsO₄ (estimated 4.7-5.0 eV) are not known with sufficient accuracy to permit a firm identification. From the estimated sputter rate of ~50 Å/min, the oxide thickness is ~400 Å for samples exposed at 50 °C and is almost twice as thick for exposures at a higher substrate temperature of T_s=150 °C. However, the oxide thicknesses obtained to date have not been sufficient to permit either x-ray diffraction analysis or detection of oxide lattice modes in the Raman spectra (see below) that could confirm the chemical composition of the oxide layer.

For oxidized III-V materials, several groups[14,15] have discussed the use of Raman spectroscopy to detect oxidation-induced disorder and the accumulation of the elemental column-V species at the oxide-substrate interface. Raman data for the n-type (110) sample on and off the atomic O beam exposed areas at a substrate temperature of 150 °C is shown in Figure 4. The symmetry-forbidden LO mode can be made observable by the presence of

Figure 4. Raman spectra using 488 nm excitation of a GaAs (110) n-type sample which was exposed to atomic oxygen at a substrate temperature of 150 °C. Spectra were taken in the center of the atomic-O exposed area and in an area outside of the atomic-O beam profile. The expected locations of crystalline metallic As TO and As

LO Raman peaks are shown as tick marks.

residual strain, roughness or disorder in the substrate. For the O-exposed surface, there is no significant decrease in the TO/LO relative intensity, indicating that oxidation has not perturbed the crystalline order of the substrate sufficiently to relax the Raman selection rules. These results contrast with those for thermal oxidation of (100) GaAs which show a strong "forbidden" LO peak as a result of substrate disorder[14].

Raman spectra of thermal oxides grown on GaAs also show strong peaks at about 257 and 200 cm^{-1} arising from the LO and TO phonons, respectively, of crystalline As at the oxide/GaAs interface. Amorphous As, if present, would produce a broad band from about 200 to 250 cm^{-1} . For substrates exposed at 50 °C and 150 °C the O-exposed areas show none of these features indicating the absence of amorphous or crystalline metallic arsenic. To the best of our knowledge, there has been very little previous work specifically aimed at detecting free As at native-oxide/GaAs interfaces. Grunthaner et al.[16] have used XPS chemical depth profiling to study 30-40 Å thick native oxides on n-type (100) samples and find a thin layer of free As at the interface but none within the oxide. Apparently, oxidation by high kinetic energy atomic oxygen does not produce metallic As in either the oxide or at the oxide/GaAs interface.

The effect of substrate temperature on oxide thickness and quality was examined by exposing two n-type (110) GaAs samples to a 2.8 eV O-atom beam for 5 hours each while holding the sample temperatures at 45 °C and 160 °C. The resulting oxides were analyzed using XPS, sputter depth profiling, and Raman spectroscopy. XPS showed that the oxide layer formed at both temperatures is fully oxidized and the sputter profiling indicates that the oxide formed at 160 °C is approximately twice as thick (600-1000 Å) as the oxide formed at 45 °C. Raman spectroscopy indicates no substrate disorder and no As in the oxide or interface region. These results indicate that increasing the substrate temperature will provide a thicker high-quality oxide when employing a high kinetic O-atom reactant. This is contrary to high temperature thermal oxidation processes where high substrate temperature alters the oxide stoichiometry by preferential evaporation and decomposition of As oxides.

The environmental and chemical stability of the oxide layer was investigated by looking for changes in the XPS spectra over a one month time while leaving the oxide exposed to the laboratory air environment and by observing the oxide etch characteristics in a 1% Br₂/Methanol solution. XPS analysis performed immediately after growing the oxide layer and months later show no observable changes in the spectra indicating that the oxide is quite stable in the usual laboratory environment. An attempt was made to remove the oxide film by etching the sample in a 1% Br₂/Methanol solution. However this etching procedure led to the preferential removal (i.e., differential etch) of the unoxidized region, leaving the O-atom beam oxidized region largely intact. These observations indicate that the oxide layer is passivating and chemically stable unlike native oxides or thermal oxides grown at high temperature.

CONCLUSION

Thick, uniform, and fully oxidized layers on GaAs have been formed by exposure to a high kinetic energy atomic O beam. The oxidation process has a minimal effect on the crystalline order of the substrate and results in no detectable (by Raman spectroscopy) levels of either crystalline or amorphous elemental As at the oxide-GaAs interface. Increasing the substrate temperature from 50 °C to 150 °C roughly doubles the oxide thickness when the exposure time is ~5 hours. At 50 °C, reducing the exposure time decreases the oxide thickness and the apparent oxidation state. The oxide layer has a much reduced etch rate with a 1% Br₂/Methanol solution compared to the unoxidized GaAs substrate. Experiments are in progress to establish

the influence of such parameters as surface orientation, carrier type and concentration, and atomic oxygen beam kinetic energy and flux during O exposure on the oxide layer formation kinetics. Additional characterizations of the oxide layers are in progress to establish whether the interface state density is sufficiently low to be of interest for insulating layers in electronic devices.

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