Oxide Passivation of Photochemically Unpinned GaAs

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between substrate and incident ion. While RIE is capable of producing nearly vertical wall profiles, altering the wall shape necessitates changes in gas chemistry or adjustment of reactor discharge conditions. Our method for gaining an insight on how contouring of etched features might be influenced was to measure angular etching dependencies of several films and gases used in device fabrication under RIE conditions. Results show that oxides and nitrides have an angular dependence resembling a cosine function at low CHF$_3$ energy but develop a high-angle etch maximum when ion energy is increased. However, the substrates Si or poly-Si, having lower selectivity to CF$_3$ species, give curve shapes resembling a sputtering yield. Photoresist also resembles a sputtering yield under fluorocarbon discharge, but O$_2$ and NF$_3$ ions show chemical etching of photoresist. Inert ions that have typical sputtering curves provide a method for changing the angular etch curve shape when combined with a chemical etchant.

Angular etching correlations produce three distinct etch characteristics: (i) curve shapes that show material removal purely by chemical etching, in which ion sputtering is minimized; (ii) physical removal through knock-on bombardment, in which yields show a maximum rate at more oblique angles of incidence; and (iii) mixed combinations of physical-plus-chemical or chemical-plus-chemical removal. Condition (iii) provides a method whereby angular dependence is purposely changed during the total etch time. Differential etching is accomplished by admixing two gases during the course of an etch by using computer programming of mass flow controllers. An example is given for a computer controlled flow of NF$_3$ into primary etchant, CHF$_3$, resulting in predetermined etchback of photoresist and oxide to produce a tapered sidewall with rounded corners. Differential etching provides an additional technique for influencing shapes of wall profiles.

Knowledge of angular etching correlations from ion interactions on materials provides data necessary for accurate simulation of the etch process. Using angular yield data, a computer algorithm was developed to model time-rate of material loss and graph two-dimensional profiles similar to our experimental results. By applying etching simulations based on angular yield data, one can delineate formation of oxide sidewall spacers and reconstruct patterns resulting from structuring trilevel resist masks. These simulations also model RIE of contact holes (vias) based on sequential gas mixing because the angular etch interdependency of oxide and resist is known.

It is concluded that where plasma reactors are amenable to measuring angular etch dependence, an extension of modeling as outlined in this report will bridge the gap between device designers and lithography (processing) laboratories to help meet fabrication requirements.

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ABSTRACT

Using Auger electron spectroscopy and x-ray photoelectron spectroscopy we show that the unpinned GaAs is covered by a Ga$_2$O$_3$ layer with only small amounts of species containing arsenic. This oxide is formed by the consumption of GaAs during the unpinning treatment. We believe that it is this oxide that passivates the surface, allowing it to remain near flat-band for several hours in room air. The near absence of arsenic in the oxide, and the eventual repinning of the surface Fermi level supports the effective work function model of Fermi-level pinning.

Offsey et al. (1) reported that the surface of n- or p-GaAs could become nearly flat-band even in air if the surface was treated with the combination of flowing deionized water and above bandgap laser light. The sharp reduction in surface band bending was detected by a rise in photoluminescence efficiency that was most pronounced at short wavelength excitation (i.e., response to blue laser light) (2). Both n- and p-type GaAs responded to this treatment, indicating that the surface Fermi level was actually unpinned, unlike other treatments where low surface recombination velocities are obtained by repinning the Fermi level near the appropriate bandedge (3). The capacitance-voltage characteristic of an Hg/PMMA/n-GaAs structure showed control of the surface Fermi level. Repinning of the surface under continuous ∼0.25 W/cm$^2$ He-Cd laser light occurs on a time scale of hours (1), while others (4) correctly note that the repinning takes longer in the dark. Although flowing water treatment by Massies and Contour (5) showed a clean GaAs surface, the fact that GaAs could remain unpinned in room air for some time suggested that the surface was protected by a passivating layer.

In this paper (6) we describe a modified photowashing treatment. We characterize the surface oxide which appears to protect the unpinned GaAs surface.

Experimental

The original photochemical process (1) is labor intensive, results in a small unpinned area that is not visibly identifiable, and requires care in using the ∼100 W/cm$^2$
laser. We tried and adopted for most purposes a similar process designed to produce large area unpinned surfaces. The GaAs wafer is mounted on a photoresist spinner. Tap fed deionized (DI) H₂O is sprayed onto the central area of the wafer via a PVC hose and an eyedropper nozzle. (Attempts to add oxygen to the water stream have not produced noticeable changes, perhaps because oxygen is not available in the ambient.) Light is supplied by a 300W tungsten halogen projector bulb with an integral reflector brought within several inches of the wafer.

GaAs wafers were prepared by solvent rinses followed by soaking in 1:1 H₂SO₄--H₂O and etching for 30s in freshly prepared, hot 12:1:3 H₂SO₄--H₂O₂--H₂O followed by an H₂O quench. Under projector bulb illumination, with the wafer spinning at several thousand revolutions per minute, and sprayed with water at ~10 cm³/s, a uniform, bright blue oxide film is formed in 5-10 min. The color results from interference effects, and oxides thicker than this (~100 nm) are not obtained. “Spotty” oxides often indicate surface contamination. Excessive water flow rates or insufficient illumination result in the lack of observable oxide growth.

To unpine the Fermi level at the GaAs-oxide interface, an activation step is performed following the bulk oxide growth. Illumination is continued while the H₂O stream is directed onto the wafer onto the spinner’s rotating aluminum vacuum chuck to keep the GaAs wafer from overheating. Typically several tens of seconds of illumination are sufficient. Afterward, light exposure is continued for several minutes while the wafer is spinning, allowing for surface adsorbed water but not light to remove even thick oxides containing GaAs. Surface characterization steps will unpin localized areas. If the wafer is stored in lab air prior to activation, the PL response is reduced from that of freshly prepared samples. Delays of an hour produce a significant degradation. However, the wafer can be stored in dessicated air, in liquid nitrogen, or in high vacuum for days with minimal surface contamination. Excessive water can be removed by soaking in 1:1 H₂SO₄--H₂O and etching for 30s.

The Auger electron spectrum of a ~100 nm oxide grown by the photochemical process is shown in Fig. 1. Arsenic (in all chemical states) is detected at a ~2% level, with contributions from the oxide, the GaAs substrate, and the ambient of the epitaxy system in which the spectrum was taken. This is in marked contrast to other methods of oxidizing GaAs, such as AGW anodization (8) where the resulting oxide’s Ga to As ratio is typically not far from unity.

The x-ray photoelectron spectrum of a much thinner oxide produced by brief treatment is shown in Fig. 2. A very brief photochemical treatment preceded a ~15 min air exposure while the sample was transported to the analysis chamber and loaded through its airlock. In this spectrometer the x-rays were not monochromatized, and as a result elemental and gallium-bonded As are not resolved. However, the core level shifts for oxides of arsenic are substantial enough to allow their differentiation from elemental As and GaAs. Results from curve fitting of the spectrum indicates that the oxide is ~1.2 nm thick and is composed of 90% Ga₂O₃ and 10% As₂O₃. By using different incident angles, the oxides of arsenic are found to be evenly distributed through the thin oxide. Air exposure of the thin oxide may be responsible for the relatively large amounts of As-containing oxides present in the film.

Thus, the following picture of the oxide growth process emerges (6, 9, 10). GaAs is oxidized through the availability of minority carriers and water. The oxides of arsenic are preferentially washed away by the water flow because their solubility in near-neutral water is far greater than that of the oxides of gallium (10). Oxygenation of the water, through the air ambient or through electrolysis, increases the solubility of any unoxidized arsenic. Using the spinner with water but not light removes even thick oxides containing GaAs, producing a clean surface (5). This growth mechanism suggests that the oxide should be porous. This is substantiated by the rapid response of the GaAs PL to changes in the gaseous ambient. The photochemical treatment may unavoidably leave trace quantities of species containing arsenic in the film. Only very small quantities are required to produce repinning through reactions that create elemental arsenic at the GaAs-oxide interface (11), such as 2GaAs + As₂O₃ → Ga₂O₃ + 4As. This may explain why the GaAs-oxide interface eventually repins in the dark, even in inert ambient (He, N₂, vacuum).

![Fig. 1. Auger derivative spectrum of a ~100 nm thick oxide grown by the photochemical process. The primary constituents are gallium and oxygen. Carbon is not detected. Arsenic is present at the ~2% level.](image1)

![Fig. 2. X-ray photoelectron spectrum of a 1.2 nm thick oxide resulting from brief photochemical treatment. The peak at ~-21.6 eV is Ga from GaAs. The peak at ~-23 eV is Ga from Ga₂O₃. The peak at ~-43.3 eV is As from both GaAs and any elemental As. The peak at ~-46.9 eV is oxidized As. The oxide composition is 90% Ga₂O₃ and 10% arsenic oxides.](image2)
A dense Ga$_2$O$_3$ film could have desirable insulating properties. Experimentally, we have been unable to produce good insulating films with our photochemical technique. Perhaps due to the oxide's alleged porosity, capacitance measurements do not reflect classical metal-insulator-semiconductor behavior. Anodic oxides of GaAs are typically satisfactory insulators. We have formed anodic oxides by the AGW process (8) and attempted to unpin the Fermi level at the anodic oxide-GaAs interface using our photochemical process. But in order to unpin the interface Fermi level, we find that we must remove all the anodic oxide (for instance by using a higher water flow rate and little or no illumination) whereupon the photochemical process will work but a poor insulator is obtained. If we start with our photochemical oxide on GaAs, anodizing it results in rapid repinning.

Conclusions

The growth of Ga$_2$O$_3$ films on photochemically unpinched GaAs is documented. The Offsey et al. technique is modified to produce large-area treated wafers. Attempts to create good insulating films with unpinched GaAs interfaces have been unsuccessful. The recently reported hydrated sodium sulfide treatment (7), in certain aspects of its unpinning and repinning behavior, resembles the photochemical oxides.

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18O Tracer Study of Si Oxidation in Dry O$_2$ Using SIMS

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ABSTRACT

Si oxidized sequentially using $^{18}$O$_2$ and $^{16}$O$_2$ isotopic tracers was studied in detail to investigate the oxidation mechanisms for dry $O_2$ oxidation. Analyses of these samples with SIMS provided detail profiles of the $^{16}$O and $^{18}$O concentration in the oxide. At 1 atm and 1000°C we found $^{18}$O reacted both at the surface of the oxide as well as at the interface. A subsequent anneal of the $^{18}$O oxides revealed that $^{18}$O in both regions of the oxide isomerizes, especially for thin oxides. Even for thicker oxides the situation is even more complex. It appears that a single activation energy diffusion coefficient have been observed (1-3). A major effect is clearly related to the variation of the oxide structure with growth temperature which leads to nonlinear Arrhenius plots for the parabolic rate constant. For thinner oxides, the situation is even more complex. It appears that a strictly interface reaction limited mechanism originally proposed by Deal and Grove (4) is inadequate in explaining the observed effects (4-14), even though this treatment works well in explaining oxidation in steam.

Although the investigation of silicon oxidation in "dry" $O_2$ has proceeded for a number of years, there is still considerable controversy concerning the dominant mechanisms, especially for thin oxides. Even for thicker oxides which exhibit nearly parabolic growth behavior, substantial deviations from a strictly single activation energy diffusion coefficient have been observed (1-3). A major effect is clearly related to the variation of the oxide structure with growth temperature which leads to nonlinear Arrhenius plots for the parabolic rate constant. For thinner oxides, the situation is even more complex. It appears that a strictly interface reaction limited mechanism originally proposed by Deal and Grove (4) is inadequate in explaining the observed effects (4-14), even though this treatment works well in explaining oxidation in steam.

These factors led us to begin an investigation of silicon oxidation in "dry" oxygen (15, 16) using $^{18}$O$_2$/$^{16}$O$_2$ tracer methods. In these studies, oxides were grown initially in $^{16}$O$_2$ and then in $^{18}$O$_2$. The $^{16}$O and $^{18}$O profiles could then be measured and used to determine effects related to the appropriate growth mechanisms. In addition to our work of

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