Wet Etching of $\text{Al}_2\text{O}_3$ for Selective Patterning of Microstructures Using $\text{Ar}^{+}$ Ion Implantation and $\text{H}_3\text{PO}_4$

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Abstract

A new etching method for single-crystal $\text{Al}_2\text{O}_3$ is proposed using $\text{Ar}^{+}$ implantation and $\text{H}_3\text{PO}_4$ chemical etching. Photolithographically defined patterns are transferred into sharp structures on the wafer surface by selectively removing the damaged material. A double implantation of $\text{Ar}^{+}$ at 50 keV followed by 180 keV was performed on all samples, using a dose of $2 \times 10^{15}$ ions/cm$^2$ for the low-energy implant. Doses of $2 \times 10^{15}$, $2 \times 10^{16}$, and $4 \times 10^{16}$ ions/cm$^2$ were used for the 180 keV implant. Scanning electron microscopy and atomic force microscopy were used to characterize the pattern obtained, while transmission electron microscopy and Rutherford backscattering channeling analysis were employed to study the implanted layer. Under the conditions investigated, both the etchable range (90 to 160 nm) and the etching rate (1 to 7 nm/min) were found to be strongly correlated with the implanted dose. Sharp and uniform interfaces between etched and unetched regions were obtained, forming steps with an average slope of 30 to 45°. The proposed method offers high selectivity, lack of contamination of the substrate, and compatibility with standard processing.

Introduction

Over the last several decades $\text{Al}_2\text{O}_3$ maintained the interest of researchers because of its distinctive mechanical, thermal, optical, and electrical properties. $\text{Al}_2\text{O}_3$ films have been widely used as insulating layers or coatings because of their chemical stability and hardness. Moreover, silicon-on-sapphire (SOS) devices attract considerable attention on $\text{Al}_2\text{O}_3$ from a technological point of view, particularly due to their true compatibility with the planar technology of silicon. $\text{Al}_2\text{O}_3$ thin films have also been used for heteroepitaxially grown Si-on-insulator (SOI) structures for sensor applications, as a protective layer for reactive sputtering removal of the damaged layer and turns out to be dose dependent, as shown in Fig. 1. After implantation the resist was removed from the surface using boiling acetone followed by plasma etching or chemical etching using $\text{H}_3\text{PO}_4$ at room temperature. This cleaning procedure was necessary because the ion beam produces hardening of the photoresist. Finally, the samples were wet etched using $\text{H}_3\text{PO}_4$ at 180°C.

The height of the resulting step was routinely measured by means of a mechanical stylus profilometer with 5 nm resolution. Scanning electron microscopy (SEM) with X-ray microanalysis, and atomic force microscopy (AFM) were used to characterize the patterned regions after the etching. The damage profile was measured by means of the Rutherford backscattering (RBS) channeling technique using 2 MeV He$^{+}$ ions. Transmission electron microscopy (TEM) analyses were performed on cross-sectioned samples using a Philips CM 30 microscope operating at 300 kV.

Results and Discussion

Etching profiles.—The etching process causes the removal of the damaged layer and turns out to be dose dependent. Photolithography was used to pattern on the $\text{Al}_2\text{O}_3$ surface suitable masks preventing damage in selected areas. Micrometric structures with sharp interfaces were defined on the wafer surface using the proposed process.

Experimental

The present results refer to sapphire samples cut from 3 in. wafers, (1102) oriented (r-plane), with surface roughness around 2 nm. Photore sist 600 nm thick allowed selective damaging of the substrate. Two different patterns were used, one formed by $50 \times 50$ μm areas separated by 200 μm, the other consisting of 50 μm lines separated by 5 μm. All samples were double implanted at room temperature with $\text{Ar}^{+}$ at 50 and 180 keV (Table I). While the first implantation principally affects the near surface of the wafer and allows the first stages of the chemical reaction to proceed, the second one damages the inner layer. The dose rate was estimated to be around $10^{13}$ ions/cm$^2$ s. The implantation angle was 8° from normal to the surface to avoid channeling. Due to shadowing effects, a difference between opposite sides of patterned structures is expected, as shown in Fig. 1.

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Table I. Dose and energies used to implant the samples with $\text{Ar}^{+}$ at room temperature. The measured maximum etchable depth and the mean etching rate are also given.

<table>
<thead>
<tr>
<th>Sample</th>
<th>50 keV, dose (ions/cm$^2$)</th>
<th>180 keV, dose (ions/cm$^2$)</th>
<th>Saturation depth (nm)</th>
<th>Etching rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$2.0 \times 10^{15}$</td>
<td>$2.0 \times 10^{15}$</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>$2.0 \times 10^{15}$</td>
<td>$2.2 \times 10^{15}$</td>
<td>150</td>
<td>2.5</td>
</tr>
<tr>
<td>C</td>
<td>$2.0 \times 10^{15}$</td>
<td>$4.0 \times 10^{15}$</td>
<td>100</td>
<td>7</td>
</tr>
</tbody>
</table>

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dependent. Figure 2 shows a SEM micrograph of the Al₂O₃ surface after 40 min etching for sample B. The sample is tilted in order to better evidence the surface features. The step produced by etching is clearly visible and appears to be straight and uniform. The region where implantation was masked remains unetched (top side of the picture) while the implanted area was etched away, thus forming a 150 nm height step. At this final stage of the process, all samples show the same morphology.

The sample surface was studied by AFM. Figure 3 shows the effect of the implantation angle on the final structure, resulting in different slopes of the edges at opposite sides of the pattern. Numerical differentiation of the profiles also revealed this difference.

Typically the side corresponding to the resist step facing the ion beam (Fig. 3a) appears sharper than the shadowed one (Fig. 3b). The maximum boundary width (measured between 10 and 90% of the full height) was around 300 and 500 nm for the unshadowed and shadowed sides, respectively. For the former, the maximum slope found is 40 to 45°. At the end of the whole process, the surface roughness at both sides of the step is that of the virgin substrate (~2 nm).

Figure 4 displays the etched depth vs. time for three different 180 keV implantation doses. Both the saturation depth and the average etching rate increase with increasing Ar⁺ dose. For the lower dose used the maximum etchable depth is around 90 nm, while for a dose an order of magnitude greater it reaches 150 nm. For a further twofold increase in dose, the corresponding etchable depth is 160 nm, showing a trend toward saturation.

The average etching rate varies from 1 nm/min for a dose of 2 × 10¹⁶ ions/cm² to 7 nm/min for 4 × 10¹⁷ ions/cm². The unimplanted areas of Al₂O₃ remain unetched at least for etching times of the order of 1 h, as shown by the time dependence in the saturated region for all samples. As no evident rounding of the corners appears before the saturation level is reached, extremely high selectivity is introduced by this method.

**Damage profiles.**—RBS-channeling analyses indicate that the damage mainly consists of point defects or amor-

![Fig. 1. Sketch of the implantation geometry.](image)

![Fig. 2. SEM micrograph of the transferred pattern onto an Al₂O₃ surface for sample B after 40 min etching. The arrow indicates the higher edge of the step.](image)

![Fig. 3. AFM profile (—) across the (a) unshadowed and (b) shadowed interface for sample B after 40 min etching; numerical derivative analysis of profiles (—•—) is also shown.](image)

![Fig. 4. Etched depth vs. time for samples A, B, and C.](image)
phous clusters. To further elucidate the relationship between dose and damage induced by Ar implantation, the defective fraction was calculated from RBS spectra (Fig. 5). The effect of the 50 keV implantation stage, common to all samples, is to produce a defective fraction of about 0.7 in the first 30 nm (a defective fraction equal to 1 corresponds to a fully damaged or amorphous layer). As for the second implantation, increasing doses produce an increase of the defective fraction in the 50 to 200 nm region up to a saturation value of about 0.7, thereby forcing the damage profile to expand deeper into the sample. Figure 6 shows a TEM cross-sectional micrograph for sample B. As indicated by selected area diffraction analyses, the TEM profile evidences two highly defective regions (dark areas). The relative position of the damaged layers is well correlated with the defective fraction profile of Fig. 5, therefore confirming the RBS results. Both the overall behavior of the damage profile and the saturation value of the accumulated damage are in agreement with previously reported results for Al2O3 implantation with Cr at room temperature.12

The comparison between the damage profiles and the etching vs. time data produces three relevant features of the process: (i) the etching becomes effective only when the defective fraction exceeds 0.4, below which the etching rate is negligible, at least in the time scale investigated; (ii) the increase in the etchable range is a consequence of the widening of the damaged profile; and (iii) the etching rate increases with the amount of damage. Thus, to obtain optimal etching parameters, both the energy and the dose of the incident beam should be tuned.

Etching mechanisms.—During the process of ion implantation, collisions with the lattice produce disorder in the crystal. As a result, the implanted layer is highly defective, including distortion and breaking of the Al2O3 bonds. The weakening of the structure allows the selective etching of the crystal, which otherwise is very stable against any chemical etchant. It is known that H3PO4 is able to evidence dislocations and other defects in sapphire,4 and it was very effective in etching the implanted layer. The fast kinetic of the etching process is probably due to the same oxidation state displayed by P and Al, permitting the kinetic of the etching process is probably due to the same oxidation state displayed by P and Al, permitting the kinetic of the etching process is probably due to the same oxidation state displayed by P and Al, permitting the kinetic of the etching process is probably due to the same oxidation state displayed by P and Al, permitting the kinetic of the etching process.

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Some relevant features of the etching process come into view from the study of the boundary between implanted and unimplanted areas. Surface roughness measurements evidence the swelling produced by the Ar+ implantation, resulting in a step of about 30 nm for 4 × 1016 Ar+ cm2. Assuming a uniform ion distribution in the implanted layer, a volume expansion of about 15% can be estimated. Therefore, the etching process is expected to be positively affected by the stress profile located at the interface. On the other hand, symmetry considerations suggest that the lattice rearrangement during the etching is less favored at the interface, where the atoms on the virgin side are already in a stable configuration. Consequently, the available number of distorted or broken bonds at the boundary is higher than in the bulk of the implanted region, thus enhancing the etching rate at the border. Therefore, both physical and chemical reasons call for an enhanced etching rate at the implanted virgin interface. This effect was evidenced by AFM profiles of samples at early stages of the process, where an increase in the etching rate up to a factor of 3 for the 4 × 1016 Ar+ dose was measured. The spatial extension of this zone is about 5 μm. As the process continues, the saturation depth is reached in the remaining damaged region.

The enhanced etching effects are particularly evident when patterned lines are close enough to allow fast etching regions to overlap (i.e., closer than 10 μm, as in the case of the 5 μm-implanted lines). Figure 7 shows a tape of damaged material abruptly detached from the substrate, after 5 min etching. In this case, the measured etched range close to the interface is about 120 nm, and 40 nm in the central part of the removed zone. The typical longitudinal extension of the tapes is about 100 μm. Actually, tape detachment could be attributed to stress release and localized fast etching rate.

Conclusions

In this work, we have shown that it is possible to introduce high selectivity in (1102) Al2O3 using conventional techniques like ion implantation and standard photolithography followed by wet etching with H3PO4 at 200°C. The proposed technique can be easily employed in Al2O3 technology where micromachining is required for device fabrication.

This method is truly contamination-free, as only Ar was used, although it is not a room temperature process. It
Toward a Unified Reaction Mechanism for Chemical Vapor Deposition of Copper

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ABSTRACT

We report the reaction kinetics of copper chemical vapor deposition using H₂ reduction of Cu(hfac), H(hfac) = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. We observe a growth rate of 0.48 ± 0.07 mg cm⁻² h⁻¹ (i.e., 9 nm min⁻¹) at reference conditions of 300°C substrate temperature, 40 Torr H₂, partial pressure, and 1.8 Torr Cu(hfac). The dependence of growth rate on operating conditions can be described using a Langmuir-Hinshelwood rate expression with a numerator that is first-order in Cu(hfac), and half-order in H₂, and a third-order denominator that includes adsorption terms for Cu(hfac)₂, H₂, and H(hfac). Optimized values for the surface reaction rate constant and the reactant adsorption coefficients are determined using nonlinear regression. On the basis of the optimized rate expression, we propose a minimum-parameter reaction mechanism for Cu(hfac) reduction. The proposed rate limiting step is the surface reaction between adsorbed H and the first dissociated (hfac) ligand from adsorbed Cu(hfac), leading to the desorption of H(hfac) product. The proposed mechanism also includes the major elementary steps needed to describe the competing disproportionation reaction. In particular, the rate constant for recombinative desorption of Cu(hfac)₂ obtained in the present work is remarkably consistent with previous kinetic results for Cu(hfac)(2-butyne) disproportionation.

Acknowledgments

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REFERENCES


Introduction

Chemical vapor deposition (CVD) of copper thin films is being intensively studied as an alternative fabrication technique for interconnect metallization in future generations of deep submicron integrated circuits. Copper offers several intrinsic property advantages over aluminum, the current material of choice for metallization; these include lower resistivity, improved electromigration resistance, and increased resistance to stress-induced voidage. The CVD technique has traditionally offered several advantages over competing physical deposition methods, including the promise of improved film conformity over high-aspect ratio features and the possibility of performing selective area deposition.

Two reaction chemistries have emerged for performing copper CVD. The highest deposition rates to date have been achieved using the disproportionation of various Cu(hfac)(2-butyne), notably Cu(hfac)(VTMS).