Feasibility of atomic layer etching of polymer material based on sequential O\textsubscript{2} exposure and Ar low-pressure plasma-etching

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We describe controlled, self-limited etching of a polystyrene polymer using a composite etching cycle consisting of sequential deposition of a thin reactive layer from precursors produced from a polymer-coated electrode within the etching chamber, followed by low-pressure Ar plasma etching, which removes the oxygen-modified deposited reactive layer along with ≥0.1 nm unmodified polymer. Deposition prevents net etching of the unmodified polymer during the etching step and enables self-limited etch rates of 0.1 nm/cycle.

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Advanced semiconductor device fabrication requires approaches capable of atomic precision in deposition and etching.\textsuperscript{1–3} Atomic layer deposition (ALD) methods have been highly successful for deposition of various materials.\textsuperscript{1} Control of deposited film thickness near one atomic monolayer is based on careful choice of chemical precursors which, once adsorbed at one monolayer on the substrate, passivate the surface and prevent multi-layer adsorption. A subsequent reaction step transforms the precursor into the desired material. Experimental and computational studies examining the feasibility to realize a corresponding atomic layer etching (ALE) approach using cyclic surface passivation followed by etching of the reacted surface layer started in the 1990s (see Refs. 3–10 for selected studies). These efforts have shown that one of the key difficulties for realizing ALE is achieving self-limited etching. For ALD, etch product removal ideally takes place in a directional manner by energetic ion bombardment of the surface. Self-limited etching requires both negligible spontaneous chemical etching by the precursor used to passivate the surface and insignificant physical sputtering of the unmodified material after etch product removal\textsuperscript{3}. The second requirement has been difficult to realize consistently, and additional factors, e.g., photon induced etching for plasma environments,\textsuperscript{11} have been shown to be important for certain conditions.

Agarwal and Kushner\textsuperscript{3} described a computational investigation of ALE of silicon and SiO\textsubscript{2} using conventional plasma etching tools. They showed that self-limited etching can be achieved by careful control of chemistry and ion energies during the passivation and etching steps, respectively. Rauf et al.\textsuperscript{12} applied molecular dynamics simulations to examine the possibility of realizing ALE using nanometer-scale fluorocarbon passivation of silicon and SiO\textsubscript{2} followed by argon ion etching. They observed self-limited etching of Si for Ar\textsuperscript{+} energies smaller than 30 eV. These computational studies indicate the feasibility of achieving atomic scale precision during etching.

In this work, we explored ALE concepts on a polystyrene-based polymer using a sequential etching approach. Each etching cycle consists of a first step, where a modified surface is produced by exposing the polymer surface to O\textsubscript{2}. The oxygen is adsorbed on the surface and forms a reactive layer, especially if the polymer has already been modified by ion bombardment. This is followed by exposure of the surface to a low power argon plasma, which rapidly removes the oxygen-modified polymer surface layer by Ar\textsuperscript{+} ion bombardment. For the unmodified polymer, the net etching rate vanishes. Real-time optical monitoring of the polymer surface during the sequential plasma etching steps support these statements.

The work was performed in a capacitively coupled plasma (CCP) reactor that uses 13.56 MHz RF power fed to the top-electrode to produce a discharge and 4 MHz RF power applied to the substrate electrode for ion energy control (see Ling \textit{et al.}\textsuperscript{13} for a more detailed description of the apparatus). A polystyrene-based 248 nm photoresist polymer spin-coated on Si wafers (~600 nm thick) was used for the work.\textsuperscript{14} Each process cycle consists of (i) O\textsubscript{2} exposure of the polymer material followed by O\textsubscript{2} exhaust from the chamber; (ii) Ar plasma used for low energy Ar\textsuperscript{+} ion bombardment of the surface, followed by Ar exhaust. For the O\textsubscript{2} exposure step, 30 sccm O\textsubscript{2} was flowed through the system for 240 s at a pressure of 40 mTorr. This was followed by 120 s pump-out which minimized the influence of O\textsubscript{2}-residual gases during the Ar etching step, but apparently left some reacted oxygen at the polymer surface (as indicated by the surface analysis measurements described below). This sequence is repeated during subsequent cycles. The conditions for the Ar plasma etching step were a pressure of 80 mTorr, 55 sccm flow, 15 s etching using a dc bias voltage of approximately −5 V by applying 20 W power to the top electrode, and 30 W power to the substrate electrode. For these conditions, it was possible to etch the oxygen-modified polymer, whereas net etching ceased for unmodified polymer. Subsequently, the chamber was pumped for 120 s (Ar exhaust). For each experiment at least 20 cycles were studied.

The O\textsubscript{2} and Ar gases were injected into the reactor through a “showerhead” top-electrode that was covered with

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a polyimide-related material (500 μm thick film of “Kapton”\textsuperscript{15}). The success of the controlled etching process was found to depend critically on the presence of polyimide-related material in the chamber. During Ar\textsuperscript{+} ion bombardment of the polymer substrate, sputtering of some polyimide-related material from the top-electrode takes place and causes a depositing flux to the polymer substrate. The polyimide-related film deposition balances etching for the Ar\textsuperscript{+} ion bombardment step once the oxygen modified layer has been removed and allows for control of the etching depth. During the O\textsubscript{2} exposure step, this reactive surface layer is modified by oxygen adsorption.

Real-time ellipsometry measurements of polymer films during ALE provided direct information on changes of film thickness and polymer surface optical properties. Figure 1(a) shows real-time ellipsometry data of the polymer layer on silicon during ALE over 20 cycles using above parameters. During the adsorption step, the Δ-values decrease, indicative of an increase of net film thickness. Molecular oxygen does not spontaneously etch carbon-based polymers at room temperature, but can be adsorbed on an activated polymer surface to form a thin layer of oxidized carbon material over unmodified polymer.\textsuperscript{16} During the Ar plasma etching step, Δ-values initially increase and remain constant subsequently.

We interpreted the ellipsometric data by optical multilayer modeling to obtain the net polymer layer thickness as a function of time. A modified top layer with a thickness of 1 nm is assumed on top of the bulk polymer film with a fixed refractive index of 1.59.\textsuperscript{17} Both the complex refractive index of the top layer and the thickness of unmodified bulk polymer were adjusted to fit the measured data. The cumulative etched thickness increases linearly with the number of ALE cycles at a roughly constant removed thickness per cycle (thickness change from the end of one cycle to the end of the next). The excellent reproducibility and nearly constant etching depth per cycle is shown in Fig. 1(b) for 20 cycles. The figure shows that this approach enables controlled removal of less than 2 nm polymer material over 20 cycles, i.e., for one etching cycle about 0.1 nm of bulk polymer is removed (see Fig. 1(b)). This behavior is reminiscent of the approach proposed by Rauf et al.\textsuperscript{12}

Thickness change and refractive index of the modified surface layer obtained by simulation of the ellipsometry data are shown in Fig. 2 for two cycles versus time. We observe a layer thickness increase of up to 0.3 nm after the O\textsubscript{2} adsorption step. The simulated thickness values show rapid etching during the first few seconds of the Ar etching step. This can be explained by easy volatilization of the layer formed on the polymer layer. Subsequently, the etching rate decreases and then vanishes. To achieve the goal of net etching of only
modified polymer material requires careful control of Ar\(^+\) ion energy along with an additional carbon flux. Once the plasma contacts unmodified polymer, a balance of etching and deposition of polyimide-related material prevents further net etching of the polymer film.

The behavior of the refractive index of the surface layer is consistent with this picture. During removal of the oxygen modified polymer surface layer, both real and imaginary part of the refractive index increase, mirroring the densification of the polymer by ion bombardment and formation of graphitic layer.\(^{16}\) The decrease of both the real and imaginary part of the refractive index seen during the O\(_2\) adsorption cycle reflects the reaction of oxygen with the densified surface carbon layer.

The dependence of etching behavior on gas flow rate (from 30 to 100 sccm), bias voltage (from floating potential to \(-50\) V), exhaust time, O\(_2\) gas exposure time, and gas pressure was explored. These tests showed that the bias voltage during the etching step and O\(_2\) gas flow rate during the exposure step were the most significant factors for achieving controlled, self-limited etching. Figure 3 shows the influence of bias voltage on polymer etch rate during the Ar plasma step. The etch rate depends strongly on bias voltage, which determines the energy distribution of the incident Ar\(^+\) ions, and therefore the sputtering yield of unmodified polymer (and also affects the sputtering rate of polyimide-related material on the top-electrode). Self-limited etching is seen for a time-averaged bias voltage of about \(-5\) V, which corresponds to a maximum ion bombardment energy of \(\approx 25\) eV (see Fig. 3, which shows data from several experiments). Ion energies must be high enough to counteract the redeposition of polyimide-related material and remove the oxygen-modified carbon material formed during the previous cycle. If the ion energy is too small, deposition of sputtered polyimide-related material dominates over etching, causing film growth on the polymer surface.

Polymer surfaces after O\(_2\) adsorption and Ar etching were also examined using X-ray photoelectron spectroscopy (XPS) after transferring samples from the CCP chamber to the XPS analysis chamber through a cluster system under ultra high vacuum conditions. In Fig. 4, we show XPS difference spectra\(^{19}\) of carbon and oxygen 1s photoemission peaks obtained by subtracting spectra after the O\(_2\) adsorption step from spectra obtained with samples after the Ar\(^+\) etching step (electron take-off angle is \(20^\circ\)). Surprisingly, the XPS data show only slightly more oxygen after O\(_2\) adsorption. Additionally, the positive carbon peak difference spectrum is also unexpected since it indicates a more carbon-rich surface after the O\(_2\) adsorption step than after Ar\(^+\) ion bombardment, which appears inconsistent with the ellipsometry data. It is possible that this is an artifact of the XPS measurement, owing to the labile nature of the surface layer after O\(_2\) adsorption and the transfer of the sample into a UHV environment. Alternatively, high reactivity of the carbon surface after Ar\(^+\) sputter may cause adsorption of residual oxygen during chamber pumpout.

Sputtering of polyimide takes place during the argon plasma etching step and can lead to deposition of carbon-rich species on the polymer surface. It is also possible that residual carbon-rich species from the polyimide adsorb on the polymer surface during Ar exhaust, and possibly during O\(_2\) exposure. This may explain in part the thickness increase seen during these phases. It appears that the sputtered species have higher carbon content than the polymer surface after low energy Ar\(^+\) ion bombardment. Hishmeh et al.\(^{20}\) and Biederman et al.\(^{21}\) showed that during polyimide sputtering, both imide and ether groups of the pristine polyimide molecules are destroyed. After sputtering in an argon atmosphere, a graphitized polyimide surface was detected.\(^{22}\) Therefore, it is plausible that the plasma generated species produced from polyimide-related material may be carbon-rich.

Sputtered carbon-rich species of polyimide-related material deposited onto the polymer surface likely exhibit high reactivity and bond O\(_2\) admitted to the chamber during the adsorption step, consistent with the increased oxygen content after the adsorption step. Experiments performed without polyimide on the top-electrode did not show self-limited etching and also exhibited less oxygen adsorption on the polymer surface. Adsorption of oxygen and formation of a surface layer with reduced density during the O\(_2\) adsorption step is consistent with the behavior of both thickness and refractive index seen in the ellipsometry measurements. More work is needed to explain the XPS measurements.

We conclude that concurrent deposition of a carbonaceous material during Ar\(^+\) ion bombardment and subsequent O\(_2\) exposure enables controlled removal of ultra-thin polymer layers. Future work will address the question if direct injection of passivation film precursors tailored for diverse materials during or after the argon etching step can be used...
to produce the reactive surface layer rather than by sputtering polyimide-related film precursors from a biased surface of the etching chamber. Additionally, an important question is if the current demonstration of controlled nanoscale etching can be extended from planar surfaces to three-dimensional structures, where adsorption and etching are expected to strongly vary for horizontal and vertical surfaces.

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