Remote plasma treatment of Si surfaces: Enhanced nucleation in low-temperature chemical vapor deposition

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The nucleation density on Si(100):H is increased by two orders of magnitude after exposing the surface to a remote argon plasma. We study HfB2 growth from Hf(BH4)4 and MgO growth from Mg(DMDBA)2 plus H2O. In the latter case, pretreatment allows the growth of MgO films with an rms roughness below 0.5 nm, whereas in absence of plasma treatment no nucleation is observed. The plasma does not damage the substrate and is compatible with microelectronics technology. We propose that H desorption is the key mechanism leading to nucleation enhancement, and that remote plasma activation is likely to be generally applicable. © 2009 American Institute of Physics.[doi:10.1063/1.3243980]

Nucleation conditions affect both the microstructural quality and surface roughness of deposited thin films. Sparse nucleation is a problem in many atomic layer deposition (ALD) and chemical vapor deposition (CVD) processes,1,2 and it impedes the growth of pinhole-free films at the low film thickness required in microelectronics and nanotechnology, e.g., diffusion barriers.

Several methods to enhance nucleation have been reported: (i) altering the surface termination to aid precursor adsorption,1,3,4 (ii) bombarding the surface with energetic particles that may be chemically reactive5 or nonreactive,3 and (iii) abrading the surface.6 Although each of these approaches is effective within its context, all are generally system-specific and may give rise to undesirable changes in the substrate surface.

Here we describe the use of a noble-gas remote plasma (RP) to activate the surface of H-terminated silicon by creating reactive sites that promote rapid nucleation with very high density. The RP flux does not damage the substrate and is fully compatible with current microelectronics technology. We believe that this approach can also be applied to oxide, carbide, and nitride substrates terminated with H or OH groups. We demonstrate nucleation enhancement for the two following low temperature CVD processes: HfB2 growth from the single-source precursor Hf(BH4)4 (Refs. 7 and 8) and MgO growth from Mg(DMDBA)2 and H2O, where DMDBA=H3BN(CH3)2BH3.

Hydrogen terminated Si(100) substrates are prepared following standard procedures.9,10 The RP treatment and film growth by CVD are performed in a UHV chamber pumped to a base pressure of 10−9 Torr as described elsewhere.7 During film growth, the total gas pressure in the chamber is ∼10−5 Torr, such that gas phase collisions are negligible; therefore, any changes in the film growth kinetics are due to surface (not gas phase) effects. The RP is generated by flowing 15 sccm of ultrapure argon gas in a Pyrex tube of 3.6 mm inner diameter that passes through an Evanson microwave cavity operated at 2.45 GHz at a net power of 60 W (90 W forward and 30 W reflected). Film growth is begun shortly after the substrate treatment.

Figure 1 shows that the RP treatment has a significant effect on the nucleation behavior of the Hf(BH4)4 precursor at a substrate temperature of 275 °C. The nucleation density measured by atomic force microscopy (AFM) is significantly higher on a substrate treated for 30 s (∼1015/cm2) compared with an untreated substrate (∼6×1010/cm2) (Fig. 1). The corresponding AFM line scans show that the film on the pretreated surface is much smoother [Fig. 1(b)]. An analysis of the height distribution function P(h) clearly shows that coalescence has been reached in the pretreated substrate [Fig. 1(c)]. The P(h) of this sample follows a Gaussian distribution with no distortion due to the substrate. The P(h) of the untreated substrate, on the other hand, is dominated by the substrate contribution (a single sharp peak at a height of 1 nm) and HfB2 islands account for the tail extending to h > 5 nm.

Rutherford backscattering spectroscopy analysis of the untreated and pretreated samples gives Hf area densities of 2×1014 and 9×1015/cm2, respectively. This 45-fold increase in the amount of deposited film is due to enhanced nucleation upon pretreatment. This finding is confirmed by in situ spectroscopic ellipsometry measurements. The nucleation delay, i.e., the time lapse between the initial exposure of the surface to the precursor and the first appearance of nuclei, is 45 s on untreated surfaces but less than 15 s on RP-treated surfaces (Fig. 2). The data are fit to a multilayer model comprising a surface roughness layer, bulk, and Si substrate. All optical constants are known.8

Significant differences are also observed at longer deposition times. The AFM surface roughness after 2 min growth is 2.1 and 0.8 nm for the untreated and pretreated samples, respectively. Furthermore, XPS reveals that the film on untreated substrate has not reached coalescence even after 8 min, whereas on the treated substrate the Si 2p peak is no longer detected after 45 s of growth, indicating a continuous...
HfB$_2$ film with no pinholes. The enhanced nucleation also has a significant impact on the microstructure: a 50 nm thick HfB$_2$ film on a treated substrate has a more refined columnar structure and a smoother surface than film grown on an untreated surface (Fig. 3).

In the case of the MgO growth from Mg(DMDBA)$_2$ and H$_2$O at 275 °C and a precursor pressure of $2 \times 10^{-5}$ Torr, the MgO film does not nucleate at all on an untreated substrate. Upon RP treatment, nucleation occurs readily (Fig. 4), but only if the RP is left on during the nucleation stage. We hypothesize that by continuously creating new active sites, the plasma counteracts the repassivation of the surface due to the adsorption of reactants or reaction byproducts. The dense nucleation results in the growth of extremely smooth MgO films: the rms roughness is only 0.35 and 0.50 nm for film thicknesses of 10 and 30 nm, respectively (Fig. 4, inset).

For both the HfB$_2$ and MgO CVD processes described above, the steady-state film growth rate does not change when the plasma is switched on. This shows that no unintended plasma enhanced CVD process takes place, and that the fluxes or energies of the plasma-generated species are not sufficient to drive growth-related surface reactions at significant rates. Current-voltage measurements on a flat probe at the substrate position, for biases up to $\pm 18$ V with respect to the chamber ground, yield linear I-V plots with an equivalent resistance of 27 $\text{M}\Omega$, indicating the absence of space charge effects or a plasma sheath. With the substrate at ground potential, which is the case for film growth, a net positive current density of 50 nA/cm$^2$ flows from the plasma to ground.

The most likely mechanistic interpretation for the observed nucleation enhancement is RP-stimulated H desorption, which would create a large population of dangling bonds on the substrate surface. The mechanistic role of dangling bonds in promoting nucleation is well known: scanning tunneling microscopy (STM)-induced desorption of hydrogen can enable spatially defined CVD that is restricted to bare (dehydrogenated) areas.$^{11}$ However, it is remarkably difficult to determine which plasma species is responsible for the observed effect. This is a common problem in plasma-based experiments because (i) it is nearly impossible to create a source that emits only one species, or (ii) to vary the flux of one species without varying others, and (iii) sophisticated apparatus is needed to quantify the fluxes. We and other authors have shown that a change in the operating conditions of the discharge (i.e., power and pressure) affects the densities of all the species involved as well as the energy distribution function of the charged species.

In previous experiments, reaction pathways for hydrogen desorption have been identified for photons,$^{12}$ metastable atoms,$^{13-16}$ electrons, and ions,$^{17}$ all of which are generated inside the plasma. In our experimental conditions, we can rule out the possibility that the surface activation is due to electrons. The cross section for H desorption is small for electron energies below 20 eV, and the flux of charged species measured at the substrate is small, as noted above.$^{17}$
Similarly, we can rule out that surface activation is due to photons from resonant transitions, because these are scattered due to self-absorption and subsequent reemission (the mean-free path of Ar 4s photons is <1 mm at 1 mTorr Ar pressure).

Argon metastables, however, are likely candidates for the surface activating species. Using a time-of-flight mass spectrometer, Kurahashi and Yamauchi\textsuperscript{18} analyzed the desorption of H\textsuperscript{+} from Si(111) surfaces stimulated by a pulsed He plasma, and concluded that the species responsible for desorption were fast neutrals and He\textsuperscript{+} metastables. Neither the desorption of neutral H nor the fluencies and the yields of the different processes were reported. A similar study showed that He metastables can desorb H\textsuperscript{+} from a hydroxyl terminated Na/Ni(100) surface.

To conclude, exposure of a H-terminated silicon substrate to the flux from a remote Ar plasma is an effective means to activate chemically reactive sites, presumably by H desorption, such that the nucleation density is very high during the thin film growth by CVD. This effect enables the growth of fully coalesced ultrathin films that are pinhole-free and smooth. The RP treatment does not require elevated substrate temperatures and is fully compatible with damage-sensitive technologies. Finally, there is considerable potential for extension of this approach: on the source end, the use of He would provide higher excitation energies; on the substrate end, RP treatment also may activate –OH terminated substrates and be applicable to ALD processes. Due to the multiplicity of fluxes emanating from the plasma source, further work is needed to determine the mechanism responsible for the activation of surface sites.

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\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{untreated_and_treated.png}
\caption{Field emission SEM micrographs of 50 nm thick HfB\textsubscript{2} films grown under untreated and plasma pretreated conditions.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{thickness_graph.png}
\caption{(Color online) Evolution with time of the thickness of MgO film grown under untreated and plasma treated conditions, as determined by \textit{in situ} ellipsometry. Inset: AFM topography of 30 nm thick MgO film grown under plasma treated conditions.}
\end{figure}

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