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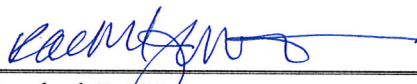
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## Etching of Tungsten and Tungsten Silicide Films by Chlorine Atoms

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### ABSTRACT

Thin films of tungsten and tungsten silicide were etched both within and downstream from a  $\text{Cl}_2$  plasma discharge at 200 mtorr pressure and temperatures below  $150^\circ\text{C}$ . When samples were positioned downstream from the discharge, etching proceeded solely by chemical reaction of the film with chlorine atoms. Without a discharge, molecular chlorine did not etch tungsten or tungsten silicide. Downstream and in-plasma tungsten etch rates were approximately equal at  $110^\circ\text{C}$ , but the chlorine atom etch rate dropped more rapidly than the in-plasma etch rate as temperature decreased. The chemical reaction between chlorine atoms and the tungsten film was proportional to the gas phase Cl atom mole fraction. A pretreatment consisting of either a dilute hydrofluoric acid dip or a short plasma etch cycle was necessary for atom etching of tungsten silicide films. The etch rates of tungsten silicide in  $\text{Cl}_2$  plasmas were approximately an order of magnitude higher and less temperature sensitive than those in the downstream (atom) configuration.

The patterning of tungsten and tungsten silicide for microelectronic circuits has been accomplished by a variety of halogen-based dry processing etching techniques (1-8). Publications on the patterning of these materials using chlorine have only summarized the effects that the process parameters have on the anisotropy, etch rate, and selectivity (5). The limited results suggest that the etch rate of tungsten is related to the concentration of chlorine atoms, Cl, produced by either laser irradiation (8) or gas-phase electron impact dissociation (5) of molecular chlorine,  $\text{Cl}_2$ . However, the etching process was controlled empirically and thus is not based on a fundamental understanding of the etching mechanism.

Control of thin film etching processes during microelectronic device manufacture is often difficult. In large part, the difficulties arise from the complexity of RF glow discharges, coupled with plasma-film interactions. One method of simplifying the etch chemistry of these processes is to utilize an upstream discharge to generate reactive atoms for etching. Since ion, electron, and photon bombardment are absent in this configuration, the pure atom etch chemistry can be studied. Comparison of downstream etching with in-plasma or discharge etching then generates insight into the role of the plasma. Furthermore, such investigations yield fundamental information concerning atom reactions with materials. In this paper we present results on the chlorine atom etching (downstream or flowing afterglow reactor configuration) and  $\text{Cl}_2$  discharge etching of tungsten and tungsten silicide thin films.

### Experimental

The reactor used for plasma etching (in the discharge) has been described in an earlier publication (5). The flow reactor was modified for atom etching by connecting a discharge and flow tube upstream from the etching reactor. A schematic of the system can be found in Ref. (9).

An upstream RF discharge was used to dissociate  $\text{Cl}_2$  molecules into Cl atoms, which then passed through a flow tube into the reactor where they reacted chemically with tungsten or tungsten silicide samples without the influence of the discharge. Power was supplied by a Tegal

Corporation 300W RF generator and matching network to the upstream discharge via two 1.0 cm wide copper bands that were placed around the 3.8 cm diam quartz discharge tube. Spacing between the bands was 1.0 cm. A metal box enclosed the discharge area to ensure RF shielding and to facilitate forced air cooling of the tube. The 3.8 cm diam Pyrex flow tube contained two  $90^\circ$  bends to prevent light from the upstream discharge from reaching the reactor and thus the photomultiplier tube. The flow tube was coated with Halocarbon Corporation 1200 wax to minimize recombination of Cl atoms. The tubes and reactor were connected using MDC Corporation glass to metal Kwik-Flange adapters.

Samples were placed inside the 2.6 liter Pyrex reactor chamber on a temperature controlled 2.5 cm diam anodized aluminum rod that served as the lower electrode for plasma etching experiments. Rod temperature was varied from  $25^\circ$  to  $150^\circ\text{C}$  using heating tape and an Omega Engineering Incorporated Model 650/660 controller. In order to reduce the surface area for atom recombination and thus increase the atom concentration at the sample surface, the upper electrode was removed during tungsten atom etching experiments.

Molecular and atomic chlorine traveled approximately 60 cm from the discharge section to the sample location. The chlorine flow rate was controlled by a needle valve and measured with a rotameter. Vacuum was provided by a liquid nitrogen cold trap and a Busch Corporation Lotos corrosion resistant mechanical pump. The pressure in the reactor (200 mtorr) was established by a throttling valve at the exit from the reactor and was monitored by a capacitance manometer.

The gas phase chlorine atom concentration at the position of the sample was measured by titration with nitrosyl chloride (10-13). The NOCl titrant (Matheson) entered the reactor approximately 7 cm upstream from the sample location through a manifold to disperse gas evenly throughout the flow cross section. Flow rate was regulated by a needle valve and measured with a Tylan FM 360 mass flowmeter. Monel and Teflon were the materials used for the NOCl delivery system. A Hamamatsu R1928 photomultiplier tube with a Melles Griot 03FIV008 filter was used to monitor the 550 nm emission (chemiluminescence) resulting from the recombination reaction of chlorine atoms (9).

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