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Temperature Effects and Optical Emission Spectroscopy Studies of Hydrogen-Based Plasma Etching of Copper

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Optical emission spectroscopy (OES) and substrate temperature variation studies have been performed on Cu etch processes based on hydrogen (H_2) plasmas. Temperature was varied between −150°C and 100°C. Gas phase Cu emission was detected during the H_2 plasma etch processes. The correlation between Cu etch rate and Cu emission intensity trends as a function of temperature suggests that the Cu removal mechanism changes over the temperature range investigated. The hydrogen-Cu interaction chemistry plays a critical role in the etch process, suggesting that copper hydrides are likely etch products.

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Copper (Cu) has long been recognized as a superior interconnect material relative to aluminum (Al) in microelectronic devices and integrated circuits (ICs) due to the lower resistivity possible (1.7 μΩ-cm vs. 2.7 μΩ-cm).[1] However, implementation of Cu interconnects is most important at small feature sizes; unfortunately, the inability to plasma etch Cu at low temperatures has been a major impediment to the development of a fully plasma-based etch process. Specifically, the lack of volatile etch products for Cu at temperatures less than 180°C led to the introduction of damascene technology for Cu patterning in 1997.[2] In this process, the intermetal dielectric layer is patterned followed by Cu electroplating into the trenches/vias in order to avoid the need for Cu plasma etching.

In recent years, a critical size effect problem has arisen for damascene Cu lines. That is, the resistivity of Cu increases significantly with decreasing line width in the sub-100 nm regime.[3–6] This effect is due to sidewall and grain boundary scattering of electrons. Larger Cu grain sizes can mitigate part of this limitation. However, although Cu grain growth should be possible upon elevated temperature annealing of Cu lines, grain growth is frustrated by impurities due to the electroplating and polishing processes.[7] A driving force therefore exists to develop a completely vapor phase low temperature plasma etching process for Cu.

A number of studies on plasma etching of Cu have been reported; these efforts have invoked halogen-based plasmas, generally at temperatures above 180°C.[8–13] Some reports have reduced the temperatures required by supplying energy in another form such as activation by laser,[14] UV,[15–19] or infrared radiation.[20,21] In addition, a two-step approach successfully removed Cu at room temperature by first chlorinating Cu in a halogen-based plasma and then removing the $CuCl_x$ or $CuBr_x$ by immersion in a dilute HCl solution.[22] However, none of these approaches have demonstrated a low temperature etch process for Cu suitable for sub-100 nm device generations that utilizes only plasma process steps.

Previously, we developed a two-step plasma etch process for Cu at low temperature (room temperature and below) which includes a Cl_2 plasma step followed by a H_2 plasma step.[23] Based upon the realization that the H_2 plasma step is the limiting step in this etch process, the feasibility of performing Cu patterning with a H_2 plasma was described[24] and preliminary mechanistic studies reported.[25] Results demonstrated clearly that H_2 plasma-based etching of Cu at low temperature (∼10°C) must involve a chemical as well as a physical component. In this paper, optical emission spectroscopy (OES) and etch temperature studies that offer further insight into this low temperature Cu etch process are described.

Experimental

Cu films with thicknesses of 100 nm (for 1 cm^2 sample etch studies) and 200 nm (for 4″ wafer etch studies) were deposited by e-beam evaporation (CVC E-Beam Evaporator) onto (100) silicon wafers that had been coated with 20 nm of titanium to promote Cu adhesion to silicon. Four inch diameter Cu-coated silicon substrates were used for OES studies or were sectioned into small samples ∼1 cm^2 for etch studies.

Both blanket and masked Cu films were studied. The blanket Cu films were characterized by XPS and SEM. Except for surface oxygen, no other impurities were detected in these films; XPS data and SEM images have been reported previously.[23]

Masked films used SiO_2 (∼150 nm) as the mask layer. The SiO_2 film was deposited in a Plasma Therm PECVD (plasma enhanced chemical vapor deposition) system with 400 sccm (standard cubic centimeters per minute) SiH_4 and 900 sccm N_2O as precursors; the substrate electrode was heated to 250°C, the power applied to the electrode was 25 W, and the pressure was maintained at 900 mtorr during the deposition process. Mask patterns were generated by fluorine-based plasma etching in a Plasma Therm SLR ICP (inductively coupled plasma) reactor; the etch gas was a mixture of 5 sccm Ar, 28 sccm CO_2, and 15 sccm C_4F_8, RF1 (power applied to the platen) was 80 W and RF2 (power applied to the coil) was 400 W, while the process pressure was maintained at 5 mtorr.

Most of the plasma etch studies of thin Cu films were performed in an ICP reactor (Oxford Plasmalab System 100 ICP-RIE) located at Oak Ridge National Laboratories. The substrate temperature was varied between −150 and 100°C by using a liquid nitrogen cooled chiller and a built-in heater connected to the substrate electrode. Single step H_2 plasma etch[24] processes were performed. The H_2 gas flow rate was 60 sccm and the reactor pressure was maintained at 20 mtorr. The radio frequency power applied to the ICP coil (RF2) was 1800 W, whereas the power applied to the substrate (RF1) was 100 W. Analogous Cu etch studies over the temperature range of −150 to 100°C were performed in an Oxford Plasmalab System 100 ICP-RIE reactor located in the Nanotechnology Research Center (NRC) at Georgia Tech. Limited temperature variation studies were also performed in a Plasma Therm ICP reactor located in the Microelectronics Research Center at Georgia Tech) that was employed in the studies described previously,[23,24] to obtain data for further comparison with the temperature studies carried out in the Oxford Plasmalab Systems at ORNL and NRC. The plasma parameters used in the Plasma Therm ICP (Georgia Tech) are RF1 = 100 W, RF2 = 500 W, 50 sccm H_2 flow rate and 20 mtorr pressure. The electrode temperature was varied between 10 and 40°C.

After Cu etching, the SiO_2 mask layer was removed with a dilute HF: H_2O solution (1:50). Cu film patterns were examined with a scanning electron microscope (SEM, Zeiss SEM Ultra60). Thickness changes of the Cu layer were determined from SEM images, Wyko

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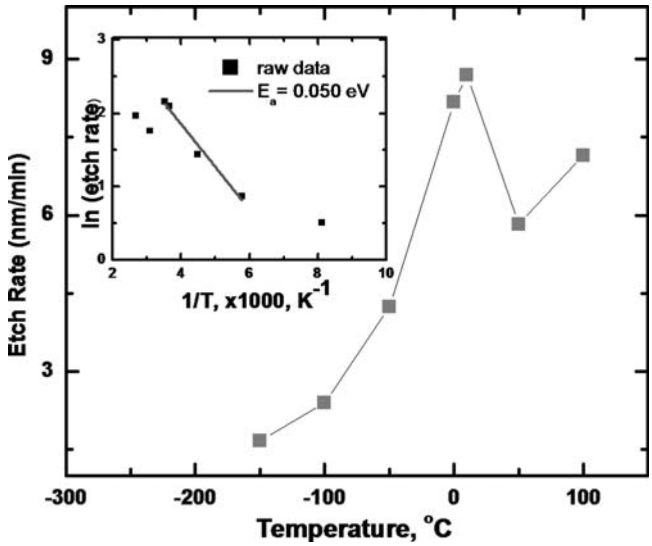

Figure 1. Cu etch rate vs. electrode temperature. Etch conditions were RF1 = 100 W, RF2 = 1800 W, 20 mTorr pressure, 60 sccm H_2 flow rate. Inset shows Arrhenius plot for Cu etch rate data.

Profilometer and Dektak 150 Profilometer data. Chemical analysis of the films and surfaces before and after plasma etching was performed using X-ray photoelectron spectroscopy (XPS). XPS spectra were collected using a Thermo Scientific K-Alpha XPS system. Optical emission spectra (OES) of plasmas during the etch processes were obtained with a Verity SD2048DL Spectroscopy system.

Results and Discussion

Effect of Temperature on Etch Rate.— Cu etch rates were determined in the Oxford ICP reactor at ORNL by measuring the etch depth of masked Cu samples (1 cm^2 size) after 10 min of H_2 plasma treatment under the conditions RF1 = 100 W, RF2 = 1800 W, 20 mTorr pressure and 60 sccm H_2 flow rate; etch rates are plotted in Figure 1 as a function of electrode temperature. As indicated in Figure 1, in the temperature range from −150°C to 10°C, Cu etch rates increased monotonically, which is consistent with higher temperatures favoring evaporation of Cu etch products. The ion bombardment flux and energy during the plasma etch process is not expected to change with the temperature. Previous studies reported that the sputter yield of Cu atoms exposed to Ar^+ ion bombardment does not increase significantly with temperature; in fact the sputter yield may display a small decrease with temperature.[26,27] In addition, our previous results[24] clearly demonstrated that sputtering with an Ar plasma at 10°C did not effectively and efficiently etch Cu films. Therefore, sputtering is not the primary cause of the etch rate increase displayed in Figure 1. Rather, such etch rate trends with temperature confirm that a strong chemical component is present in the H_2 plasma etch process.[24] It is also interesting that even at −150°C, a measurable etch rate is observed with pure H_2 suggesting that the etch product is volatile or is easily sputtered. The same etch studies were performed in the Oxford Plasmalab System 100 ICP-RIE at Georgia Tech. Etch rates measured on the two systems agreed to within ±15% and the trends in etch rates were identical to those in Figure 1.

At temperatures above 10°C, a reduction in etch rate occurs. Since this trend is reproducible in both ICP systems and is consistent with optical emission data which will be discussed later in this paper, the variation may be related to etch product instability over a certain temperature range. Specifically, if Cu hydrides are the etch products, decomposition should occur readily[28] and may affect the ability to desorb or sputter etch products from the surface. DC bias voltages for the different temperatures were essentially constant (−240 to −250 V). This observation is consistent with the fact that since the pressure and power values did not change, no substantial change in ion energy and flux should occur. These facts again suggest that the temperature effects on etch rates are related to chemical reactions between Cu and H and the ability to desorb etch products. Such results are consistent with our previous studies which indicate that pure physical sputtering using Ar plasmas is ineffective in etching Cu under the conditions used in this study, thereby offering further evidence to the importance of chemistry in this etch process.

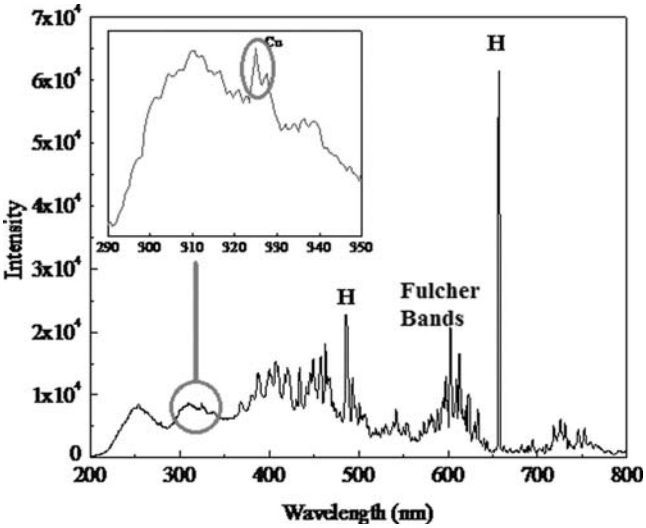

Figure 2. Optical emission spectrum of the H_2 plasma etching of Cu (4″ blanket Cu film). Plasma conditions were RF1 = 100 W, RF2 = 1800 W, 20 mTorr pressure, 60 sccm H_2 flow rate and 10°C.

The inset to Figure 1 shows an Arrhenius plot of ln (etch rate) versus 1/T. The substantial reduction in etch rate above 10°C is apparent. At temperatures between −100 and 10°C, the effective activation energy is 0.05 eV. This is a low value for strictly chemical processes (typically 0.1–2 eV), but similar to that reported for other plasma etch processes, especially when the etch process displays a strong ion bombardment component which mitigates the thermal energy requirements for reaction and product desorption.[29,30] The etch rate at −150°C deviates from the straight line shown in the inset, most likely because of the difficulty in effectively cooling the wafer. That is, estimates indicate that if the actual wafer surface temperature is at least 35°C above the measured (cooled) platen temperature, then the etch rate at −150°C would be consistent with the straight line drawn through points from 10°C to −100°C. Although we are unable to measure the surface temperature during etching, we expect that ion bombardment-induced surface heating will result in a temperature rise when the platen is being cooled to −150°C by a liquid nitrogen-cooled chiller. Due to the high thermal conductivity of Cu structures and thus the ability to conduct heat effectively,[31] it is unclear whether the temperature rises to the extent indicated by this simple extrapolation.

OES Analysis of H_2 Plasmas.— Optical emission spectroscopy (OES) diagnostics of hydrogen plasmas during the etching of blanket Cu samples (4″ wafers were used to enhance emission intensities) are shown in Figure 2 for pure H_2 plasma etching of Cu at 10°C. The hydrogen Balmer series (370 ~ 660 nm) lines are prominent in the spectrum, with high intensity atomic H lines at 656.5 nm (H_α) and 486.1 nm (H_β).[32] Cu resonance lines at 324.7 nm and 327.4 nm are also evident.[33] To a first approximation, the emission intensities may be considered indicative of changes in Cu etch rates, since little change in electron energy distribution function should occur with changes in electrode temperature. Also, as reported previously, Cu emission intensity (324.7 nm) was shown to be linearly proportional to the sputter rate of a Cu target in diode and triode systems.[34] Because CuH_x is a likely etch product, emission from a Cu hydride species is

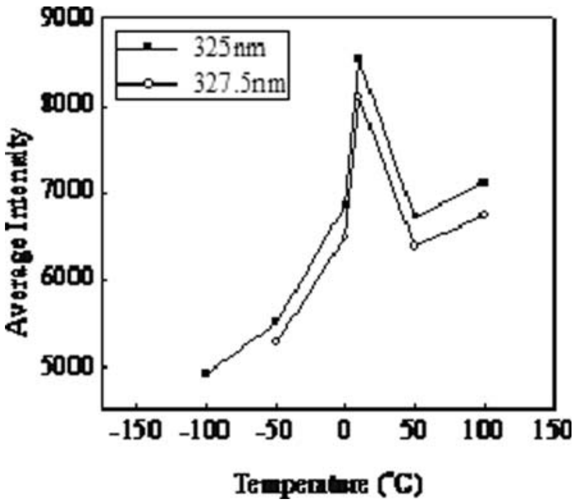

Figure 3. Average intensities of the two atomic Cu lines (325 nm and 327.5 nm) from OES during H_2 plasma etching of Cu (4″ blanket Cu film) at temperatures from −100°C to 100°C; etch conditions were RF1 = 100 W, RF2 = 1800 W, 20 mTorr pressure, 60 sccm H_2 flow rate.

expected. However, no CuH lines are detected (most intense would appear at 428 nm[33]). Furthermore, no emission lines from either CuO (most intense at 605.9 nm and 445.7 nm) or CuOH (535 to 555 nm)[35] are evident. Indeed, the volatility of these Cu compounds is quite low and therefore emission intensities are also expected to be low for species such as CuO and CuOH. The other possible etch product (CuH_2) is reported to be unstable[36] and so should undergo dissociation upon electron impact collision. In this case, Cu emission will be evident, but H emission cannot be differentiated from the etch gas background. Currently, we can only state that Cu species are in the gas phase during the etch process, but the etch product that desorbs from the surface is unknown.

Cu Emission Line Intensity as a Function of Temperature.— Because the intensities of the two Cu emission lines should be related to Cu etch rates under conditions where substrate temperature is the only variable, the average emission intensities during the sampling time of these two Cu lines are plotted as a function of electrode temperature in Figure 3, where OES data are from the etching of 4″ blanket Cu films at temperatures between −150°C and 100°C. The resolution of the OES system is 0.5 nm thus the emission lines at 325 nm and 327.5 nm in our spectrum correspond to the 324.7 nm and 327.4 nm Cu peaks reported previously.[33] The absence of OES data at −150°C and −100°C is due to the inability of the OES system to detect such low Cu emission intensities. Comparison of Figures 1 and 3 indicates that the Cu etch rate trend essentially tracks the Cu emission intensity trend between −100 and +100°C. Since the data shown in these figures were taken on different samples (data in Figure 1 are from SiO_2 masked 1 cm^2 samples while data in Figure 3 are from 4″ blanket Cu samples), these results offer strong evidence that the changes in Cu etch rates above 10°C are not due to experimental error or to an uncontrolled etch process. Although the reason for such behavior is currently unclear, the results suggest an alteration in etch mechanism at 10°C, perhaps due to a change in the specific etch product that desorbs.

Reports of CuH decomposition indicate that CuH decomposes exothermally. CuH can decompose slowly at 0°C,[28] but decomposition is rapid above 50°C;[34] above 100°C decomposition is nearly instantaneous,[28] although the majority of the decomposition occurs between 110°C and 145°C.[37] Because of the local heating induced by ion bombardment and exothermic decomposition, the surface temperature will be greater than that of the electrode set-point temperature. This enhanced energy input to the surface and concomitant temperature rise may cause decomposition of CuH so that sputtering becomes the primary mechanism for Cu removal. That is, there may be a "critical" temperature such as 10°C in our experiments, where below this temperature, Cu removal from the etching surface is controlled primarily by CuH (or other copper hydride) desorption, while above that temperature, Cu removal is more dependent upon sputtering, thereby reducing the removal rate. This assumption is consistent with the Cu etch rate behavior shown in Figures 1 and 3, although currently, no direct evidence for this mechanism can be offered. It should be noted that if the platen temperature is raised significantly above 100°C, removal of Cu may be assisted thermally in addition to sputtering effects.

Little information regarding the CuH decomposition enthalpy is available. Nevertheless, if we assume that the enthalpy of CuH formation and decomposition (ΔH^0_{dec}) are the same, the standard formation enthalpy $\Delta H^0_{298} = +21.3kJ/mol$[35] can be used as the standard decomposition enthalpy. In addition, we will assume that the specific heat capacity of bulk Cu applies to thin films: $C_{p,m} = 24.47 J \cdot mol^{-1} \cdot K^{-1}$ (at 25 °C). However, it is likely that not all the Cu surface atoms are hydrogenated; that is, there is only a fraction of CuH in the total number of moles of Cu present. Since the atomic ratio of H:Cu has been reported to be between 0.15 and 0.25 for a solution-prepared CuH substrate,[37] we will assume that the mole ratio of CuH generated by the H_2 plasma at the Cu surface (CuH:Cu, designated by $A_{CuH:Cu}$ on surface) is 0.2. A simple calculation of the temperature increase as the result of exothermic decomposition (assuming that all energy released contributes to the temperature increase) is then given by:

$$\Delta T = \frac{\Delta H^0_{dec} \times A_{CuH:Cu}}{C_{p,m} \times (1 + A_{CuH:Cu})} \qquad [1]$$

This simple estimation yields a temperature increase ΔT of 145K (with 25°C CuH formation data,[38]). Although this value is certainly an approximation, this offers some idea of the temperature rise possible due to heating by thermal decomposition of CuH provided that all energy goes into raising the Cu temperature. Of course, the temperature may be still higher than this when ion and electron bombardment-induced heating is considered. If the CuH:Cu ratio is higher or lower than 0.2, the temperature rise could be greater or less than 145°K, respectively.

Temperature Effects Observed in the Plasma Therm ICP Reactor System.— In order to obtain additional information on the Cu etch rate trends with temperature that were observed in the Oxford Plasmalab etch systems, a few temperature studies were performed in a different ICP reactor. Specifically, the Plasma Therm ICP reactor at Georgia Tech[24] has been employed despite the fact that the controllable temperature range in this reactor is only in range of 10 to 40°C. Nevertheless, this temperature range falls within the etch rate transition regime shown in Figure 1. Electrode temperature effects have been described previously,[24] where our preliminary data suggested that no change in etch rate with temperature over the range of 10° to 40°C was evident. However, those preliminary data arose by estimation of etch rates from Cu thickness changes via SEM images (with etch masks still on the surface). Of course, the accuracy of measuring small changes in Cu thickness using SEM images is poor, especially when considering nm scale differences. The measurements performed in the current study invoked a profilometer which has a resolution <2.5 nm, to determine the etch rate. Furthermore, the measurements were performed after removal of the mask material, further improving the accuracy.

Experiments were performed in the Plasma Therm reactor at three electrode temperatures: 10, 25 and 40 °C; all the other plasma parameters remained constant: RF1 = 100 W, RF2 = 500 W, 20 mTorr pressure and 50 sccm H_2 flow rate. Masked Cu samples were the same as those utilized to generate the data displayed in Figure 1; etch rate results are shown in Figure 4. Over this small temperature range, a noticeable drop in etch rates (~1.7 nm/min) occurred, while the etch rates at 25°C and 40°C were essentially constant (10.7 and

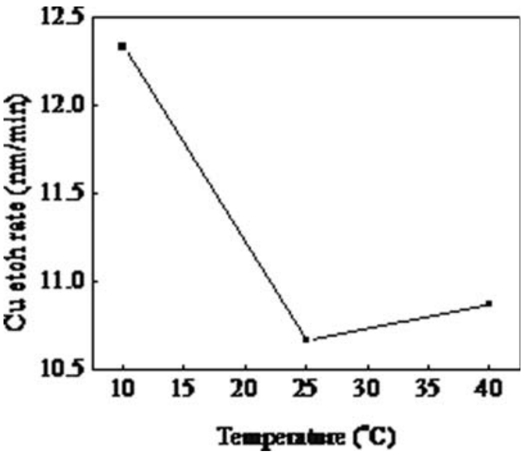

Figure 4. Cu etch rate vs. electrode temperature (Plasma Therm ICP reactor). Etch conditions were RF1 = 100 W, RF2 = 500 W, 20 mTorr pressure, 50 sccm H_2 flow rate.

10.9 nm/min) when the experimental error involved in profilometer measurements is considered. These observations are consistent with those in the Oxford Plasmalab reactors over virtually the same temperature range (Figure 1). Such results indicate that this etch rate phenomenon is not specific to a particular etch reactor, but is characteristic of the etch process.

Conclusions

Optical emission spectroscopy and etch temperature variations have been used to gain insight into the mechanisms involved in the low temperature etching of Cu in a hydrogen plasma. For a single step H_2 plasma Cu etch process, the etch rate initially (−150°C to +10°C) displayed an increase with temperature, followed by a decrease in etch rate above 10°C. These etch rate trends correlated with Cu optical emission data and were reproducible when performed in different plasma reactors (in the 10° to 40°C temperature range for one of the reactors). Such observations suggest a change in etch mechanism in the vicinity of 10°C. Atomic Cu emission lines were detected in the optical emission spectrum during etching of Cu in an H_2 plasma, which confirms Cu removal from the etching surface at low temperatures. These data suggest that CuH is a likely etch product, although direct observation of this conjecture is not available at present.

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