# LOCAL LASER INDUCED ETCHING OF COPPER FILMS BY CHLORINE

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## ABSTRACT

A focused argon ion laser was used to induce local thermal etching of copper films in the presence of chlorine gas. Raman scattering was used to follow the transformation of the copper film in situ to CuCl and $CuCl_2$. In some regimes the laser only induced transformation of copper to copper chloride, while in others the laser produced copper chloride and also desorbed it.

## INTRODUCTION

Laser-assisted dry etching of copper films is of interest because of the difficulties encountered in other types of dry etching of this important electronics material, such as by plasma etching. Recently, excimer laser assisted etching of copper films [1,2] was examined, in which the laser was used only to desorb the copper chloride produced between laser pulses by the reaction of Cu and $Cl_2$ at the substrate temperature. In this paper, we report that cw argon ion laser radiation can be used to produce local copper chloride regions on copper films in the presence of chlorine, and sometimes to desorb this product. Based on in situ Raman scattering analysis, $CuCl_2$ is the dominant product remaining on the surface in this laser-induced process. As a result of the different temperature dependence of the rate of copper chloride formation and desorption, two very different etching regions are found to occur for some experimental conditions.

In an earlier study [3], we reported that at ambient temperature Cu films (with either no oxidized layer or a several-Å-thick oxide layer) react with $Cl_2$ gas to form a film of CuCl. In contrast, focused laser heating of a CuCl-on-Cu film (partially passivated) or Cu film (passivated by a thicker oxide layer) on glass in the presence of chlorine induces a different reaction [3]. Depending on experimental conditions, the result of this laser-scanned reaction is a deposition-like line, with cross-section resembling either a bump or a bump with a trench in the middle. After subsequent removal of chlorine, in situ Raman spectra were taken of these features at 298 K. The presence of $CuCl_2$ was determined by its strong, sharp Raman peak near 282 $cm^{-1}$ and its weaker peaks near 167 and 556 $cm^{-1}$, while a broad featureless peak below 250 $cm^{-1}$ signified the presence of CuCl. In many regimes, the $CuCl_2$ peak dominates. After ex situ removal of the copper chloride by rinsing in hydrochloric acid, etched grooves remained in the copper with widths varying from 3 - 20 μm. For Cu samples with a thick overlaying oxide, there was no reaction between Cu and $Cl_2$ at room temperature. This reaction was induced only by laser heating. The relative importance of copper chloride formation and desorption during etching passivated Cu films is studied here by laser heating of Cu films in the presence of $Cl_2$.

## EXPERIMENTAL METHODS

Copper films (~ 1.5 μm thick) were deposited on glass substrates by evaporation and were then heated in air for 5 - 30 min at T = 150°C to form a thick passivation layer (passivated, ~ 100 - 200 Å copper oxide (as $Cu_2O$ [4])). Afterwards, these samples were mounted in a vacuum reaction chamber, which could be filled with $Cl_2$ gas. Once placed in the reaction chamber, the sample was viewed with a microscope through a window port in the chamber and was irradiated by a focused cw argon ion laser (4880 Å, ~ 2.2 μm full width at 1/e intensity, linearly polarized) for local laser heating and for Raman analysis. The unpolarized backscattered Raman radiation was then collected, dispersed by a triple spectrometer, and detected by an intensified diode array. The chamber was mounted on a translation stage to allow lateral scanning during laser heating. After processing, features were examined by profilometery.

## RESULTS

Profilometry analysis was performed after laser etching, both before and after the samples were rinsed in 1.4 Molar hydrochloric acid. This procedure removed the copper chloride but left the underlying Cu film alone. At the site of laser heating and localized $CuCl_2$ formation, removal of some or all of the Cu film is observed. Raman spectroscopy was performed in situ, giving spectra such as that in Fig. 1, which shows $CuCl_2$ with some evidence of CuCl.

Figure 2 plots the depth of the etched copper feature after laser scanning and hydrochloric acid rinsing as a function of laser scan speed for laser powers of 200, 300 and 400 mW, with 10 Torr chlorine pressure. When the laser power is lower than about 200 mW, the etch depth decreases monotonically with increasing scan speed. Also, the copper chloride line formed by laser heating has a cross-section of a bump with no trench, which suggests there is no desorption of the copper chloride line during "etching". When the laser power is higher than 300 mW, similar behavior is observed for slow scan speeds. However, for faster scan speeds the etched line depth now increases with increasing laser scan rates. In this regime, there is a significant desorption trench running down the middle of the deposit-like copper chloride line. However, in no case is all the copper chloride

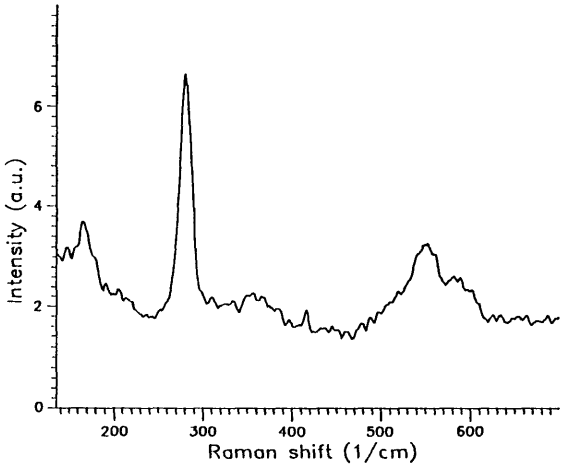

Figure 1. Raman spectrum (taken in vacuum using 20 mW 4880 Å) of a copper chloride deposition-like feature which was produced by using 70 mW of 4880 Å radiation to heat a 1.4 μm-thick copper film for 1 min in the presence of $Cl_2$ (1 Torr). The peaks at 167, 282, and 556 $cm^{-1}$ belong to $CuCl_2$, while the broad peak below 250 $cm^{-1}$ shows evidence for CuCl.

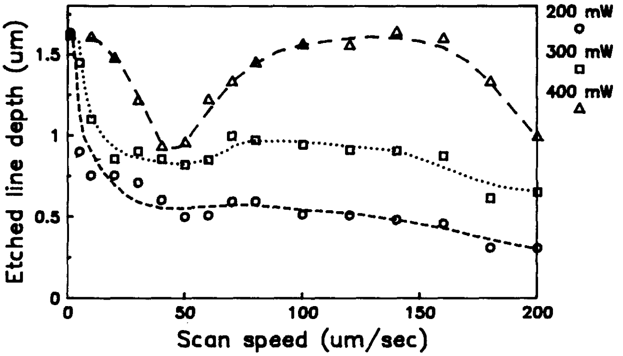

Figure 2. The depth of the etched copper features after copper chloride removal for 200 mW (circles), 300 mW (squares) and 400 mW (triangles) using 4880 Å radiation incident on a 1.6 μm-thick copper film-on glass sample (15 min oxidation at 150 °C) with 10 Torr chlorine pressure.

desorbed during laser heating. In particular, large deposits of copper chloride always remain on either side of the scanned line. At very high scan speeds the etched line depth again decreases.

In Figs. 3a and 3b, the depth of the copper etch is plotted as a function of scan speed with different chlorine pressures for laser powers of 300 and 400 mW, respectively. The change from a regime of decreasing etch depth and no copper chloride desorption at slow scan speeds to a regime with increasing etch depth with some desorption at faster scan rates is seen in many of these plots. As the pressure increases, this transition occurs at increasingly faster scan rates. The maximum etch depth decreases more slowly with increasing chlorine pressure at 400 mW than at 300 mW. Note that the initial copper film thickness is slightly different for the 300 and 400 mW experiments.

## ANALYSIS

With chlorine present, copper converts to copper chloride even with a relatively small temperature rise (~ 30 K) due to laser heating. From these experiments, it is clear that the laser must heat the film to significantly higher temperatures for the second step of etching to occur, which is the desorption of the product. The expected rates for copper chloride formation as a function of temperature are plotted in Fig. 4 at different chlorine pressures using the model presented in [1] (which has been extrapolated to higher temperatures). The expected desorption rate of copper chloride is also plotted in this figure using the data in [6]. As seen in this figure, when the chlorine pressure is 10 Torr, the temperature must be > 630 K for the desorption rate to exceed the copper chloride formation rate (7 μm/sec). This cross-over temperature decreases with decreasing chlorine pressure (to 500 K for 1 Torr).

From Fig. 4 it is estimated that a temperature rise of ~ 300 - 400 K is required to obtain the needed desorption rate of copper chlorides for a complete, one-step laser etching process. The calculation of the steady-state surface temperature rise on an evaporated copper film (1.5 μm thick) during laser heating [3] indicates that with a laser power of ~ 400 mW, the maximum temperature rise will be ~ 300 K. An incident laser power of 200 mW incident power induces only a ~ 140 K rise on the copper film, which is too low for the rate of copper chloride desorption to be competitive with the rate of formation. However, even at higher laser powers where there is desorption in the center of the laser heating area, copper chloride remains at the sides because the temperature rise is lower there.

This explains many of the observations, such as why there is relatively more desorption for higher laser powers and lower chlorine pressures in steady state. It also

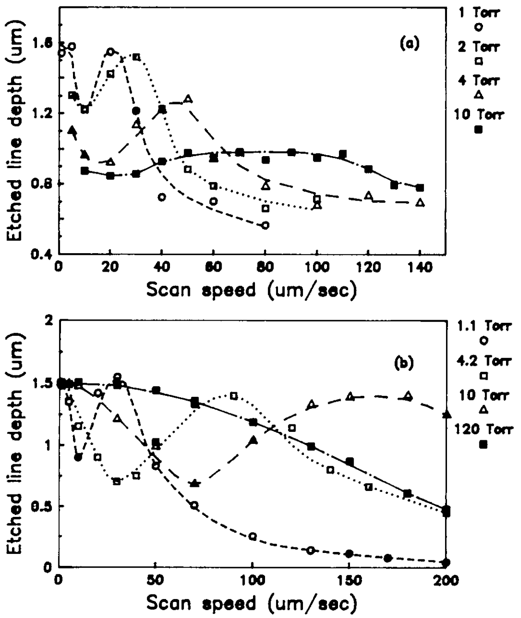

Figure 3. The depth of the etched copper features after copper chloride removal for (a) 300 mW of 4880 Å radiation incident on a 1.6 μm-thick copper film and (b) 400 mW of 4880 Å incident on a 1.5 μm-thick copper film (15 min oxidation at 150 °C) for different chlorine pressures.

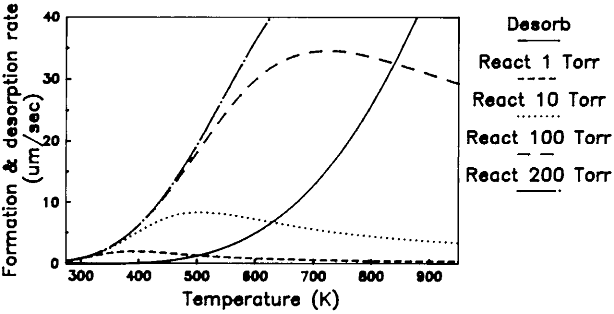

Figure 4. The formation rate (different broken lines for several different chlorine pressures) and desorption rate (solid line) of copper chloride as a function of temperature.

explains the observed dependence on scan rate. A given spot in the laser scan sees a temperature ramp from ambient temperature to the maximum laser-produced temperature and down again. The laser-induced temperature rise is in steady state for all scan rates used here. The duration of this ramp is approximately the width of the laser-produced temperature profile, which can be broader than the laser spot size [3], divided by the scan speed. For a 100 μm/sec scan speed this duration is ~ 50 msec. During a scan with high laser power, the copper is at an intermediate temperature rise, where copper chloride forms but does not desorb, before reaching the maximum temperature, where both copper chloride formation and desorption can occur. For a slow scan, the dwell time at the intermediate temperature might be so long that the copper chloride formed may be too thick to be desorbed later. This does not occur for a fast scan.

Furthermore, once a copper chloride layer forms over the copper during the laser scan, the overall process changes. The temperature profile changes with a copper chloride layer on top, which may lower the surface temperature and slow desorption. The reaction rate may also change because the diffusion of Cu cations across the copper chloride layer depends on thickness and temperature [5,7]. In the experiments described in Figs. 2 and 3, the change from a regime with no copper chloride desorption at slow scan speeds to the regime with desorption at faster scan speeds is accompanied by an increase in the copper etch depth (though the dwell time is shorter). This can be explained by a decrease in the formation rate of copper chloride when there is a copper chloride layer on the Cu. This decrease may be due to a decrease in the laser-modified temperature profile attributable to the overlayer or by the increasingly long Cu cation migration time across the layer.

## ACKNOWLEDGMENTS

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