Anomalous local laser etching of copper by chlorine

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Etching of copper films by chlorine is induced by a scanning cw laser that locally heats the film. In experimental regimes with relatively high laser power, low chlorine pressure and fast scan speed, laser etching of copper is well characterized by a kinetic model based on the calculated temperature rise. In other regimes, a thick nondesorbed copper chloride layer forms on top of the etched copper region that significantly decreases the rate of copper chlorination. Notably, in certain regimes the copper etch depth is shown to increase with increasing scan rate, which is a very unusual dependence.

Several recent studies have examined laser-assisted etching of copper films by chlorine, and have assessed the suitability of this reaction as a new dry etching process.¹⁻⁴ In these investigations laser heating was used to induce the reaction between copper and chlorine to form copper chloride products and/or to desorb this copper chloride layer. These studies have been performed over a large areas using excimer lasers¹⁻³ and in localized, micron-dimension regions using a scanning cw ion laser.⁴ In this last study, laser heating was shown to promote the chlorination of the copper film, but much of this copper chloride product (Cu- Cl_{ν}) did not desorb. Raman analysis identified this product to be mostly CuCl₂, with some CuCl. The present study shows that much of this $CuCl_{\nu}$ product can be desorbed in specific experimental regimes and that laser etching can be understood by a simple kinetic model based on laser heating. Further, in some regimes the etch depth is shown to increase with increasing laser scan speed v; whereas, normally the etch depth is expected to decrease as 1/v. This is the first reported observation of this anomalous etching dependence.

A cw argon-ion laser (4880 Å) was focused to a 0.5 μ m spot size (halfwidth at 1/e intensity) and scanned at rates up to 200 μ m/s across a copper film (1.5–2.0 μ m thick) that was deposited on a glass substrate. The top of the Cu film was oxidized in air (~100 Å Cu₂O) to passivate the surface against reactions with Cl₂ at ambient temperature. After laser scanning in the presence of Cl₂, ex situ profilometry was first used to profile the remaining CuCl_y line and then it was used to profile the line etched in the Cu film after the copper chloride layer had been dissolved by 1.5 M hydrochloric acid.

Figure 1 shows the copper etch depth versus scan speed with laser power P = 400 mW for different chlorine pressures p_{Cl_2} . Three experimental regimes can be identified. At slower scan speeds for 1.1, 4.2, and 10.0 Torr and for all scan speeds for 120 Torr the etch depth decreases with scan speed, but at a rate slower than 1/v (Regime I). At faster scan speeds (except for 120 Torr) the etch depth begins to increase with increasing scan speed (Regime II). At even faster scan speeds (except for 120 Torr) the etch depth decreases with speed as 1/v, and therefore the depth is proportional to the time that the laser dwells at a spot (Regime III). Also, in Regime I the top of the CuCl_y line formed during laser heating is flat or concave down. In Regimes II and III there are always deep trenches in the CuCl_y lines. Similar trends are observed for P = 300 mW, though the transition between these different regimes is less pronounced. In laser etching using 0.1 Torr Cl₂ (P = 500mW) the copper etch depth always varies as 1/v and there is a very deep trench down the middle of the CuCl_y line, with very little copper chloride remaining in the center (though there is a significant amount of copper chloride on either side). This is Regime III behavior.

The copper etch depth was then measured for the fastest scan speed available, 200 μ m/s, where the remaining CuCl_y line is relatively thin (Regime III), for $p_{Cl_2} = 1-10$ Torr and P = 200-700 mW, as shown in Fig. 2. The 1 and 2 Torr data (200-600 mW) are fit using a model where the reaction rate of copper with chlorine $k_r(T)$ is given by $A p_{Cl_2} \exp(-E_{act}/kT)$, where T is the local temperature at the top of the copper film during the laser scan. k_r incorporates Cl₂ chemisorption, Cl (or Cu) diffusion in Cu, and the reaction of Cu with Cl. The temperature profile T(t) during the scan is obtained by using the solution



FIG. 1. The depth of the etched copper feature after copper chloride removal for scanning of 400 mW of 4880 Å on 1.5- μ m thick passivated copper films on glass (15 min oxidation at 150 °C) using 1.1, 4.2, 10.0, and 120 Torr chlorine pressures. These runs are denoted by open circles, solid circles, open squares, and solid squares, respectively. The plotted curves were drawn through the data points for clarity.

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FIG. 2. The etched copper depth (points for experimental data, lines for model simulation) on a passivated copper film (2.0 μ m thick, 15 min oxidation at 150 °C) vs incident laser power after the film was irradiated by a scanning laser beam (4880 Å, 200 μ m/s scan rate) for different chlorine pressures. The open circles, closed circles, open squares, closed squares, open triangles, and closed triangles represent data taken at 1, 2, 3, 5, 7, and 10 Torr Cl₂, respectively.

for steady-state laser heating given by Lax,⁵ which was extended to an absorbing film (copper) on a substrate (glass), with the time t =lateral scan position/v.⁴ During a scan with P = 600 mW (2.0- μ m thick Cu film) the maximum temperature rise on the top surface is 382 K, leading to a local temperature of 677 K. All cases of potential interest are always in thermal steady state under the experimental conditions used here, including scanned laser heating of Cu films on glass and CuCl_y films on Cu films atop a glass substrate.

To determine the etch depth in this two-dimensional model, $k_r[T(t)]$ is numerically integrated in time at a given point in the scan. The thickness of the CuCl_y layer is also tracked by its rate of formation (=4 k_r , where 4 is the molar volume ratio of CuCl_y to Cu, for y = 1 or 2) and by the rate of CuCl_y desorption [$k_d = B \exp(-E_{desorp}/kT)$]. Measured values for B (3567 µm/s) and E_{desorp} (3942 K) from Ref. 6, where $y \sim 1$, are used. These parameters are expected to be insensitive to the value of y in the CuCl_y layer since CuCl and CuCl₂ have similar evaporation rates.⁷ Since diffusion of Cl (or Cu) through the CuCl_y and other details relating to the CuCl_y layer are not included in this model, this model should work best for thin CuCl_y layers (Regime III).

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The curve fits shown in Fig. 2 use $A = 324 \,\mu\text{m/s}$ -Torr and $E_{act} = 2350$ K. There is very good agreement for these Regime III data, except at high laser powers (where the rate of reaction is limited by the flux of Cl₂ to the surface) and at high p_{Cl_2} (where the CuCl_y line is becoming very thick and conditions are approaching those for Regime I). Figure 3 shows good agreement between the measured and simulated etch depth versus scan speed and at different laser powers in regimes identified as Regime III. Agreement is poor for $v < 50 \,\mu\text{m/s}$ (Regimes I and II). This model also fits all the 0.1 Torr data and the 1.1–10.0 Torr Regime III data in Fig. 1 very well.

Using these parameters, the rate of copper chloride



FIG. 3. The comparison of experimental data (points) and the model simulation (lines) of the etch line depth in a copper film on glass (as in Fig. 2) at different laser powers for 5 Torr Cl_2 . The open circles, closed circles, and open squares represent data taken at 300, 400, and 500 mW, respectively.

formation exceeds the rate of desorption for T > 300 K when $p_{Cl_2} > 1$ Torr. This explains the formation of thick (albeit partially desorbed) CuCl_y layers for the > 1 Torr runs, and the very thin CuCl_y layer in the center of the scanned line in the 0.1 Torr runs. In Regime III the copper chloride layers are too thin to affect the observed kinetics of the Cu/Cl reaction. The measured copper chloride layers are even thinner than those predicted by the model, with the central trench possibly formed by laser desorption⁴ or enhanced desorption due to energy released by the reaction.

Local laser desorption of $\operatorname{CuCl}_{\nu}$ on glass and atop a copper film on glass in vacuum has been observed during scanned laser heating (4880 Å).⁴ For laser irradiation of $\operatorname{CuCl}_{\nu}$ films on glass this occurs because there is weak absorption at this below-band-gap photon energy. Though this may be a partial explanation for the desorbed lines in Regimes II and III, it does not account for the lack of a desorption trench in Regime I.

The reaction $Cu(s) + Cl_2(g) \rightarrow CuCl_2(s)$ is exothermic by 200 kJ/mol. For a 200 μ m/s scan rate this corresponds to heat released at a rate ~ 0.03 mW, which is crease the temperature at the interface where desorption occurs (Cl₂ gas/CuCl_y) by ~ 50 K above the temperature of the critical step in the Cu/Cl reaction, then there would be competitive product desorption and the CuCl_v layer would be thin even for $p_{Cl_2} > 1$ Torr. (This is unlikely to occur in Regime I where the reaction front tends to precede the scanning laser.) The location of energy release in the actual multistep Cu/Cl reaction process is not clear, as is the site of the final Cu/Cl reaction step. If Cl atom (or ion) diffusion were dominant, the reaction would occur at the CuCl_v/Cu interface; whereas, if Cu atom (or ion) diffusion were dominant, the reaction would occur at the Cl₂ gas/CuCl_v interface. If 0.03 mW were released near the Cu film, the additional temperature rise would be insignificant (<0.1 K). If it were released near the $Cl_2(gas)/CuCl_{\nu}$

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interface, the maximum temperature at the surface would rise by at most ~ 10 K, which is still too small to promote faster desorption.

When used to model data in Regime I, this model gives Cu etch (chlorination) rates $\sim 5 \times$ times those observed. This is probably due to the rate limiting diffusion of the Cl (or Cu) reactive species through these thick copper chloride layers. The simulation shows that in Regime I the transformation of Cu to CuCl_y at any given point is essentially complete before the laser arrives there; whereas in Regime III the reaction of Cu with Cl continues after the laser has scanned past the point. Regime II, where the etch depth anomalously increases with scan speed, is seen to be a transitional region between Regimes I and III.

In their study of the thermal reaction of chlorine with copper from T = 25-200 °C with excimer laser desorption of the formed CuCl_y layers, Ritsko *et al.*¹ found that the Cu/Cl reaction occurred at a rate $k_r = C \exp(-E_1/kT)/[1 + (D/p_{Cl_2})\exp(-E_2/kT)]$, which they fit with $C = 595 \ \mu$ m/s, $D = 3.354 \times 10^4$ Torr, $E_1 = 2370$ K and $E_2 = 3865$ K. This form gives a Cu/Cl reaction rate that initially increases and then decreases with T within the temperature range of the laser heating experiments reported here, and therefore it does not fit the data presented in the current study. In Ref. 1, the high-temperature decrease of k_r was attributed to the desorption of chlorine from the surface.

In summary, it has been shown that a simple model

based on the calculated temperature rise during scanned laser heating can explain copper etching by chlorine in regimes where copper chloride desorption is at least as fast as the rate of the Cu/Cl reaction (and there is essentially no copper chloride layer at the center of the scan) or when the nondesorbed copper chloride layer is thin. Even when there is nearly complete copper chloride desorption at the center, there is still significant product buildup at either side of the scan. An unusual etching regime is observed where the etch depth (and rate) anomalously increases with increasing scanning rate. This is identified as a transition region between conditions where the overlaying copper chloride line is "thick" and "thin," corresponding to slow and fast scan rates respectively.

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- ¹J. J. Ritsko, F. Ho, and J. Hurst, Appl. Phys. Lett. **53**, 78 (1988); the updated experimental parameters from this study that are cited here are from J. Hurst (personal communication).
- ²W. Sesselmann, E. E. Marinero, and T. J. Chuang, Surf. Sci. **178**, 787 (1986); Appl. Phys. A **41**, 209 (1986).
- ³G. N. A. van Veen, T. Baller, and A. E. de Vries, J. Appl. Phys. **60**, 3746 (1986), and G. N. A. van Veen, T. S. Baller, and J. Dieleman, Appl. Phys. A **47**, 183 (1988).
- ⁴H. Tang and I. P. Herman, J. Vac. Sci. Technol. A 8, 1608 (1990), and Mater. Res. Soc. Symp. Proc. 158, 331 (1990).
- ⁵M. Lax, J. Appl. Phys. 48, 3919 (1977).
- ⁶H. F. Winters, J. Vac. Sci. Technol. B 3, 9 (1985); A 3, 786 (1985).
- ⁷R. Colton and J. H. Canterford, Eds., *Halides of the First Row Transition Metals* (Wiley, London, 1969).

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