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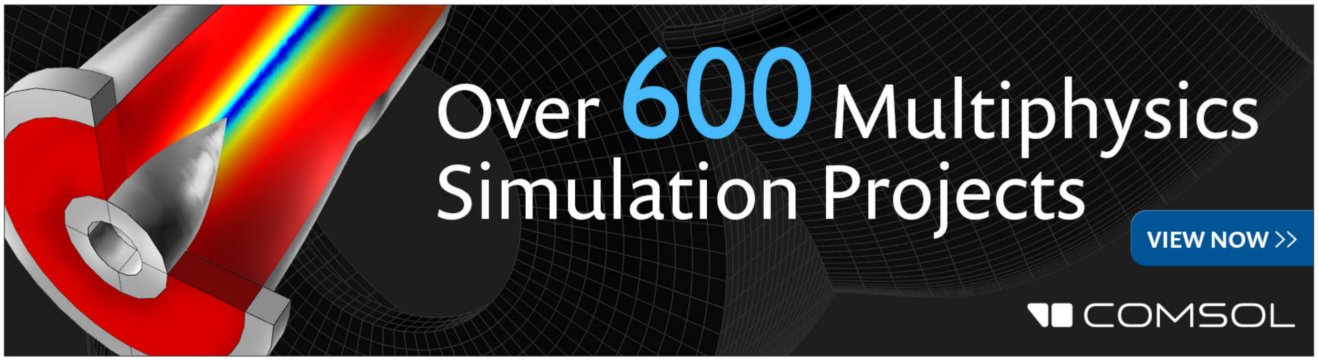

# Localized silicon etching using a laser-generated Cl source

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Ultraviolet laser photolysis of chlorine ($\lambda = 350$–$360$ nm) has been used to produce a microscopic atomic chlorine source. Crystalline silicon has been etched and deep through-wafer vias have been fabricated. The etching process has been modeled as a combination of diffusion from the Cl source, and recombination and etching at the silicon surface. Both experimental and theoretical results are given.

Laser processing of semiconductors is of interest because unique features can be obtained that are difficult or impossible to fabricate using conventional techniques. Laser photolysis of $Cl_2$ by a cw laser can be used to etch smooth vertical features in crystalline silicon without using a multistep photomasking procedure. Previously, the etching of silicon by laser photolysis of chlorine has been studied in the low-power cw[1] and pulsed[2] regimes. In this work, we examine silicon etching by laser photodissociated molecular chlorine using a high-power cw laser source operating at ultraviolet (UV) wavelengths (350–360 nm) near the chlorine absorption peak at 330 nm. We show that this photolysis scheme produces a microscopic source of chlorine atoms which can be used to produce localized etching of a silicon substrate. As a particular example we have demonstrated the etching of smooth via holes in a silicon wafer. Because of the local nature of the Cl-atom source, etching only occurs in the interior of the via into which the laser beam is directed. Since the process is driven by a photolytic mechanism, etching occurs at low temperature and the thermal damage to the surrounding silicon is avoided.

In these experiments crystalline silicon, typically $n$-type, 4–6 $\Omega$ cm resistivity, and (100) orientation, was etched in a chlorine ambient (0–600 Torr). The samples were cleaned with a standard RCA cleaning process before loading into a vacuum chamber. The etching chamber consisted of a nickel-plated, stainless-steel cell with a fused-silica window. The chamber was evacuated to $< 10$ mTorr before filling with chlorine. The 350–360 nm lines of an $Ar^+$ laser were focused with a UV-transmitting microscope objective to a spot size of 1.5 $\mu$m (FWHM) at the sample surface. The sample was located 3 mm below the lower surface of the window.

The focused beam photodissociated chlorine into reactive atomic chlorine, which diffused to the sample and spontaneously etched the silicon surface. The maximum temperature rise of the substrate has been calculated (as in Ref. 3) to be $\approx 15$ °C for the structures studied here. Therefore, thermal contributions to the etch rate can be neglected.[4]

The profile of the etched features changed with the length of exposure time. For short etching times, the features were characterized by clear crystallographic planes [Fig. 1(a)]. At longer times, the etched feature increased in size, and the straight edges of the square pattern as seen along the wafer axis were replaced by increasingly curved sides until finally a perfectly rounded perimeter was observed [Fig. 1(b)]. For long etch times, cylindrical through-wafer vias were formed. This etching development behavior is in accord with conditions which lead to reaction-rate-limited etching. The slowest etch rate is then obtained in the direction normal to the (111) planes, which are the most closely packed.[5] The (111) plane can be identified in Fig. 1(a), which shows the exposed (111) plane at an angle of $\approx 57°$ with respect to the unetched (100) surface. The features observed at longer etch times do not display a crystallographic dependence. As shown in Fig. 1(b), under conditions of long etch time cylindrical through-wafer vias with smooth sidewalls and no crystallographic features are ob-

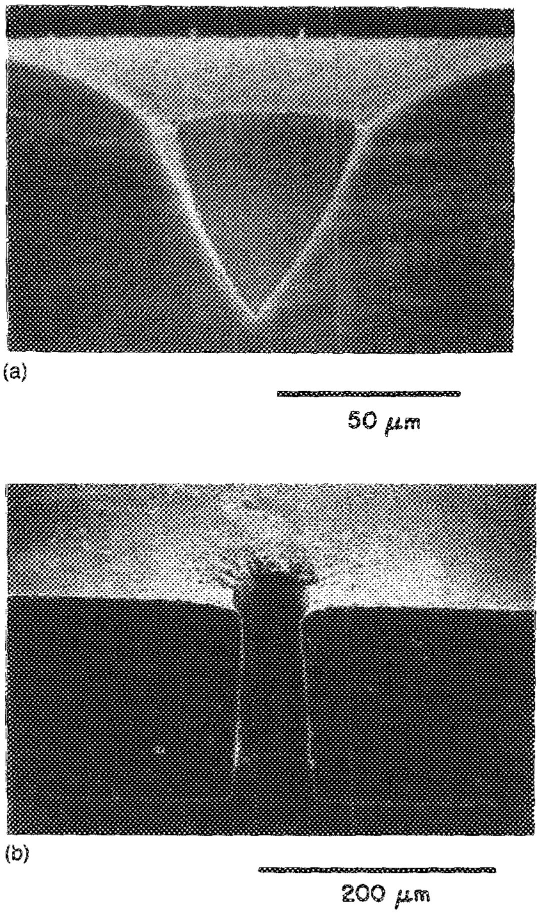

FIG. 1. (a) Scanning electron microscope (SEM) micrograph showing crystallographic dependence of etched via in silicon. The sample was (100) silicon cleaved parallel to the (110) plane. Laser power $P_L$ was 0.08 W. Chlorine pressure was 400 Torr. Etch time was 1000 s. (b) SEM micrograph showing via morphology for high-power, long etch time regime. Laser power $P_L$ was 0.48 W. Chlorine pressure was 500 Torr. Etch time was 600 s.

tained. We believe that gas diffusion effects which lead to a transport-limited reaction influence the transition between the crystallographic and noncrystallographic regimes.

To characterize the etching process as a function of laser etching parameters, we studied the development of etched via holes as a function of etch time, laser power, and chlorine pressure. For example, as seen in Fig. 2(a), the etched via area, as measured at the surface, increased linearly with time (the solid lines in Fig. 2 are based on the model given below). A similar behavior was also seen for the depth of the vias. This linear dependence persisted over a large range of etch times and laser powers, showing that via area is a good indicator of the etch rate for this Cl/Si system. Figure 2(b) shows that via area was also found to be linearly dependent on incident laser power. In contrast, a plot of via area versus chlorine pressure displayed a more complex dependence [see Fig. 2(c)]. For low pressures, via area increased roughly linearly with pressure, while at higher pressures the via area saturated.

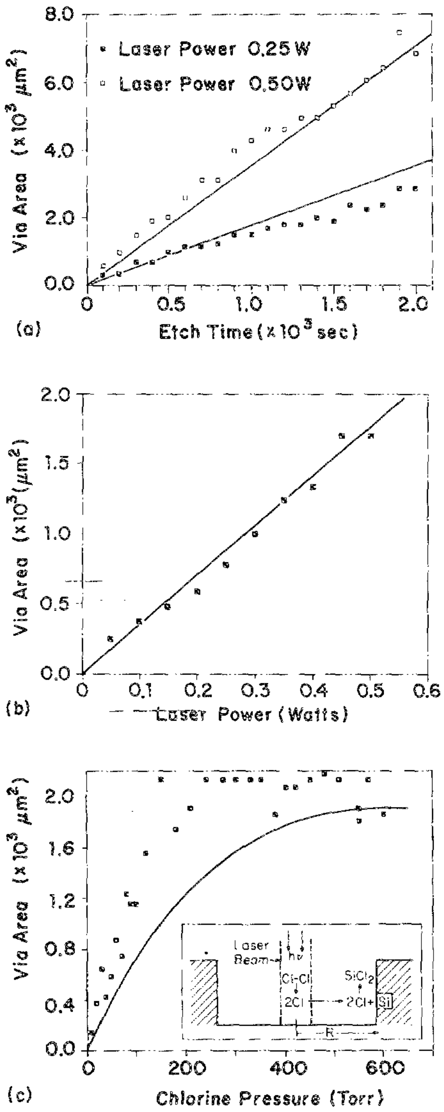

FIG. 2. (a) Etched via area (measured on surface, at entrance) vs etch time. Chlorine pressure was 400 Torr. Solid lines are model results. (b) Etched via area vs laser power. Chlorine pressure was 400 Torr. Etch time was 500 s. Solid line is model prediction. In (a) and (b) the laser power $P_L$ at the vacuum chamber was 16% of the indicated laser power. (c) Etched via area vs chlorine pressure. Laser power $P_L$ was 0.08 W. Etch time was 500 s. Solid line is model prediction. The inset shows a schematic diagram of the simplified geometry used in the theoretical model. The via is represented as a cylinder of radius $R$. The source is a cylinder in the center of the via.

To explain the data exhibited in Figs. 2(a) – 2(c) and to understand more fully the reaction physics, a model has been developed that contains the key features of the etching process. In order to obtain an analytical solution, we assumed the simplified one-dimensional via geometry shown in the inset to Fig. 2(c). Atomic chlorine is generated in the beam path by the following photodissociation process which has a peak in cross section near our laser wavelength[6]:

$$Cl_2 + h\nu \rightarrow 2Cl. \tag{1}$$

The Cl atoms created in the beam diffuse radially to the silicon surface. We have estimated the loss of Cl due to gas-phase recombination to be a subdominant effect for our relatively low-pressure conditions. At the surface Cl atoms may react with and etch the silicon or may recombine to form $Cl_2$. We will assume both the etch rate and the recombination rate to be linearly proportional to the incident Cl particle flux at the surface. This is consistent with a reaction mechanism in which gas-phase Cl atoms combine with surface-phase SiCl to produce volatile $SiCl_2$, or recombine with surface adsorbed Cl as is the case for fluorine recombination.[7] In both cases the surface-phase reactant species is readily formed. Of course other reaction mechanisms could lead to the etch and/or recombination rates being proportional to the square of the Cl concentration.[8] However, it can be shown that our model is independent of the order of these reactions, provided that the order is the same for both etching and recombination. The ratio of the etch rate to the recombination rate is the one free parameter in our model.

In order to calculate the concentration of Cl at the etching surface, the generation of Cl atoms in the beam was calculated. Absorption by $Cl_2$, for the pressures studied here, was small enough that the chlorine ambient could be considered to be optically thin in the region of the via. Thus the magnitude of the line source $s_0$ becomes

$$s_0 = 2(\alpha P_s / h\nu), \tag{2}$$

where $P_s$ is the calculated laser power at the sample surface, $\alpha(P_{Cl_2})$ is the $Cl_2$ absorption coefficient[9] in $cm^{-1}$, and $h\nu$ is the energy per photon ($h\nu \approx 3.5$ eV for $\lambda = 350$–$360$ nm). In the steady state, the continuity equation ($\nabla \cdot J = 0$) implies that the net flux of Cl to the surface at radius $R$ is $J_{surf} = s_0 / 2\pi R$. This flux is balanced by the etching and recombination processes at the sample surface:

$$J_{surf} = J_{etch} + J_{rec}, \tag{3}$$

$$J_{etch} = \eta_e n_R \bar{v}/4, \tag{4a}$$

$$J_{rec} = \eta_r n_R \bar{v}/4, \tag{4b}$$

where $\eta_e$ and $\eta_r$ are the reaction efficiencies for etching and recombination, respectively, $\bar{v}$ is the Cl atom thermal velocity, and $n_R$ is the Cl atom density at the via surface. The flux $J_{etch}$ etches the surface via the net reaction[10]

$$Si + 2Cl \rightarrow SiCl_2, \tag{5}$$

increasing the via radius at a rate

$$\frac{dR}{dt} = \frac{1}{2}\frac{J_{\text{etch}}}{N_{\text{Si}}}. \tag{6}$$

Combining (1)–(6) and integrating the resulting equation for $R(t)$ yields the following expression for via area:

$$\pi R^2 = \frac{\eta_e}{\eta_r + \eta_e}\frac{\alpha P_L \exp(-\alpha l)}{h\nu N_{\text{Si}}}t, \tag{7}$$

where $R$ is the via radius, $t$ is the etch time, $P_L$ is the laser power incident on the vacuum chamber, and $l$ is the distance between the window and the sample surface (3 mm). The dependence on chlorine pressure is through $\alpha$, which is proportional to $P_{\text{Cl}_2}$. The ratio $\eta_e/\eta_r$, the only adjustable parameter in the model, was found to be 0.011.

The experimental data plotted in Figs. 2(a)–2(c) are in good agreement with this mathematical model. Because of the linear dependence of the via area on $t$ and $P_L$ as shown in Eq. (7), the model predicts the observed linear dependence of the etched via area on etch time and laser power. The saturation that is observed in the etch rate at higher pressures is shown by the model to be explainable by absorption of the laser power in the space above the sample. Finally, the one-dimensional model assumes an infinite line source, which is appropriate over most of the via length. However, near the bottom of the wafer the beam spreading is comparable to the via diameter. This may explain two-dimensional features such as the widening of the via near the exit as exhibited in Fig. 1(b).

Finally, we have recently begun applying this UV laser etching technique to the fabrication of practical device structures. Although we could not routinely operate at high laser powers for the UV wavelengths reported here, smooth, cylindrical vias were etched through a 250-$\mu$m-thick wafer in less than 5 min at a power of 0.8 W. These vias have been employed in the fabrication of a novel low-loss fiber-optic tap.[11] In that work, laser-etched vias were shown to have good electrical properties and to be ideally suited to the insertion of optical fibers due to the matching cylindrical geometry and similar aspect ratio. With even higher power (4 W), multiline (458–514 nm) operation, through-wafer vias could be etched in silicon in under a minute using a combination of the present photolytic process and a melt-enhanced reaction studied earlier.[4]

We have demonstrated the etching of silicon using a photolytically generated source of atomic chlorine. The process has been used to form smooth through-wafer vias in silicon, and may be useful in other applications requiring a microscopic source of chlorine atoms. A model has been presented that describes the etching process as a function of etching time, laser power, and chlorine pressure, and which yields excellent agreement with experimental data.

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