of the levels to the vibration modes of the lattice atoms. The knowledge of these parameters yields a more complete characterization (or fingerprint) for a deep level than that obtained from thermal ionization data alone.

In the cases examined here, the electric field enhancement of the ionization rate is many orders of magnitude above the value which could be expected from a Poole-Frenkel barrier lowering mechanism. Only a tunneling process can account for the observations. In fact, some of our measured field ionization rates are more than seven orders of magnitude above their low-field thermal values.

An interesting feature of our theory is its ability to predict the ionization rate over wide ranges of temperature and electric field. This is valuable when DLTS results obtained for a diode made on heavily doped semiconductors (large electric fields) are to be compared with results corresponding to slightly doped semiconductors (low electric fields).

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[1] L. L. Rosier and C. T. Sah, Solid State Electron. **14**, 41 (1971).
[2] M. Martini and T. A. McMath, Solid State Electron. **16**, 129 (1973).
[3] J. M. Herman, III, and C. T. Sah, Phys. Status Solidi (a) **14**, 405 (1972).
[4] D. V. Lang, J. Appl. Phys. **45**, 3014 (1974).
[5] S. D. Brotherton and A. Gill, Appl. Phys. Lett. **33**, 953 (1978).
[6] G. Vincent, A. Chantre, and D. Bois, J. Appl. Phys. **50**, 5484 (1979).
[7] H. Lefévre and M. Schulz, Appl. Phys. **12**, 45 (1977).
[8] D. Pons and S. Makram-Ebeid, J. Phys. Theor. Appl. (Paris) **40**, 1161 (1979).
[9] W. Franz, in *Handbuch der Physik*, edited by S. Flügger (Springer, Berlin, 1956), Vol. XVII, p. 155.
[10] D. V. Lang and C. H. Henry, Phys. Rev. **B15**, 989 (1977).
[11] A. M. Huber, N. T. Linh, M. Valladon, J. L. Debrun, G. M. Martin, A. Mitonneau, and A Mircea, J. Appl. Phys. **50**, 4022 (1979).
[12] A. Mircea, A. Mitonneau, and J. Vannimenus, J. Phys. Lett. **38**, L41 (1977).
[13] A. Mircea and A. Mitonneau, J. Phys. Lett. **40**, L31 (1979).
[14] D. V. Lang (private communication).
[15] C. H. Henry and D. V. Lang, Phys. Rev. B **15**, 989 (1977).
[16] R. Stratton and F. A. Padovani, Phys. Rev. **175**, 1072 (1968).
[17] A. Onton and R. C. Taylor, Phys. Rev. B **1**, 2587 (1970).
[18] A. Onton, Phys. Rev. **186**, 786 (1969).
[19] H. C. Montgomery, J. Appl. Phys. **39**, 2002 (1968).
[20] A. Kasami, J. Phys. Soc. Jpn. **24**, 551 (1961).
[21] A. Mitonneau, A. Mircea, G. M. Martin, and D. Pons, Rev. Phys. Appl. **14**, 853 (1979).
[22] B. K. Ridley, J. Phys. C **11**, 2323 (1978).
[23] D. Bois, A. Chantre, G. Vincent, and A. Nouailhat, Inst. Phys. Conf. Ser. **43** (Institute of Physics, London, 1979), p. 295.

Plasma etching characteristics of sputtered $MoSi_2$ films

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Plasma etching of sputtered $MoSi_2$ films using CF_4/O_2 mixtures was studied in a barrel-type reactor. The etch rate in pure CF_4 was very low ($\lesssim 100$ Å/min) and insensitive to applied power. The addition of a small percentage ($< 10\%$) of O_2 dramatically increased the etch rate. For $CF_4/4\%\ O_2$, and etch rate of ~ 920 Å/min was measured at 100 W. A near-linear etch rate dependence on rf power was observed, indicating that the controlling factor is the generation rate of etching radicals. For $CF_4/8\%\ O_2$, the etch rate nearly doubled and showed saturation at high rf power, indicating the increased role of the surface reaction rate. Postdeposition anneal results in a 10–20% decrease in etch rate. An etch rate selectivity of 14–22 for $MoSi_2$ vs SiO_2 and of 2–3 for doped poly-Si vs $MoSi_2$ were measured.

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It has been recently shown[1] that the refractory metal silicide $MoSi_2$, which has a sheet resistance about ten times less than that of doped polysilicon, can be used as a gate electrode in short-channel MOSFET's. In this paper, results are presented on the plasma etching characteristics of sputtered $MoSi_2$ films. Plasma etching technology has been extensively studied[2-4] because it is a critical process in the fabrication of micron and submicron integrated circuits.

$MoSi_2$ films were deposited by dc magnetron sputtering onto oxidized silicon substrates in an MRC 603 system. Argon was used to sputter the silicide from an alloy target of stoichiometric composition. Typical deposition parameters were 3 kW power and 10 μm Ar pressure. The typical film thickness was ~ 3500 Å. For device fabrication,[1] the $MoSi_2$ film is usually annealed in Ar at 1000 °C for 1 h in order to lower its sheet resistance. Positive photoresist (Shipley 1470) was used to produce a step in the $MoSi_2$ films for etch rate determination.

A barrel-type plasma etcher (Tegal 421) was used in conjunction with various CF_4/O_2 mixtures. The initial am-

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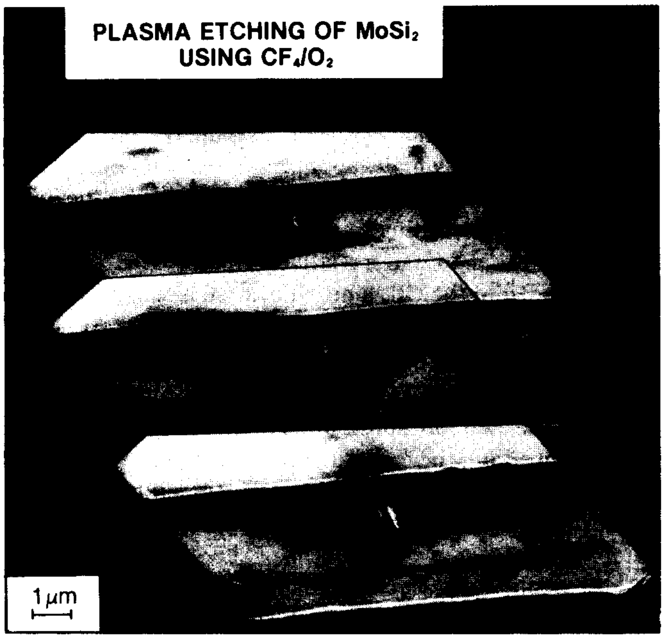

FIG. 1. SEM microphotograph of a bar pattern of plasma-etched $MoSi_2$ lines.

bient temperature was set at 75 °C. During the reaction process (~1–20 min), a temperature rise of 10–20 °C was measured in the chamber. The reactor was first evacuated down to a pressure of 0.05 Torr and then a controlled gas flow was introduced from calibrated gas mixture cylinders. Fine-line definition was reproducibly achieved down to a ~1-μm linewidth. The etching characteristics of both as-sputtered and annealed films were studied. Owing to the reactor configuration and the isotropic nature of the chemical etching process, the edge profiles of Fig. 1 reveal undercutting approximately equal to the film thickness (~3 kÅ). Consequently submicron (~0.7 μm) lines show an unacceptable profile. However, the use of a planar-type plasma etcher or reactive ion etcher can result in more vertical sidewalls, though probably at the expense of etching selectivity.

The etch rate was characterized as a function of rf power, CF_4/O_2 ratio and ambient pressure. In Figs. 2(a) and 2(b), etch rate is shown vs rf power for as-sputtered and annealed films, respectively. In the case of pure CF_4, the etch rate was very low ($\lesssim$ 100 Å/min) and insensitive to applied rf power. As expected, the addition of a small percentage of oxygen resulted in a dramatic increase in the etch rate. For $CF_4/4\%\ O_2$, an almost linear etch rate dependence on rf power was observed over the 25–100 W range [Fig. 2(a)]. At 100 W, an etch rate of ~920 Å/min was measured. Beyond 100 W, the etch rate starts to saturate. Increasing the oxygen percentage to 8% enhanced the etching but resulted in a nonlinear dependence and pronounced saturation at high rf power (> 100 W).

Postdeposition anneal of $MoSi_2$ films resulted in a 10–20% decrease in the etch rate, as illustrated in Fig. 2(b). For example, at 100 W and $CF_4/4\%\ O_2$, the etch rate was reduced from 920 to 740 Å/min. This is consistent with the observed[1] amorphous to crystalline phase transition which occurs during the anneal.

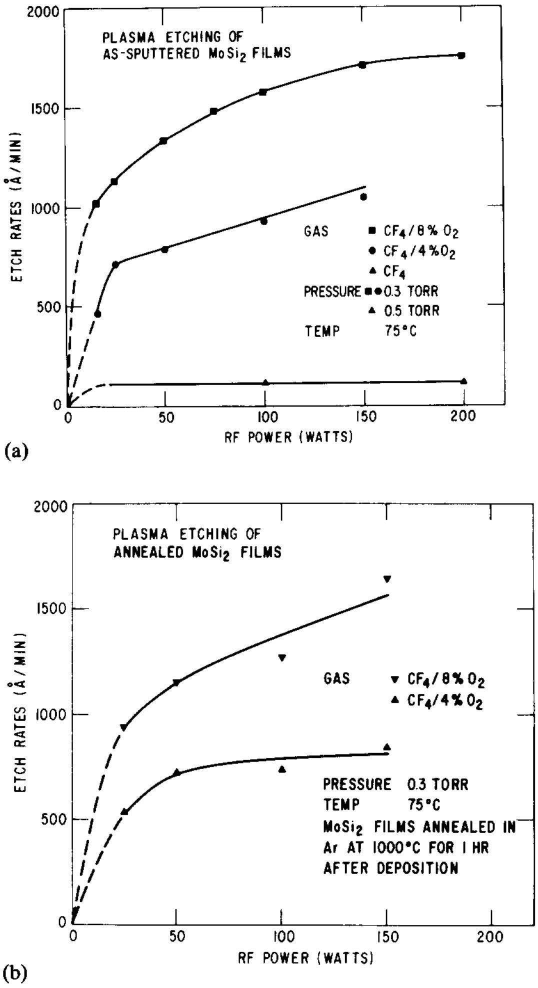

FIG. 2. $MoSi_2$ etch rate vs rf power: (a) as-sputtered films, (b) annealed films.

The dependence of the silicide etch rate on ambient pressure was studied mainly for as-sputtered films. As can be seen in Fig. 3, the etch rate dependence has two regimes. Between 0.15 and 0.25 Torr, the $CF_4/8\%\ O_2$ etch rate at 100 W is linear with pressure and thus probably mass flow limited. Above 0.25 Torr, the etch rate is constant. This can be attributed to the combined effect of limitations in reaction kinetics and evaporation of resultant products.

Since the plasma etching process is to be used in the definition of $MoSi_2$ interconnects and electrodes, usually over a silicon dioxide layer, the etch rate selectivity of $MoSi_2$ vs SiO_2 is a critical parameter. As shown in Fig. 4, the etch rate selectivity is better than an order of magnitude, ranging from 14–22. The rf power and the oxygen concentration ap-

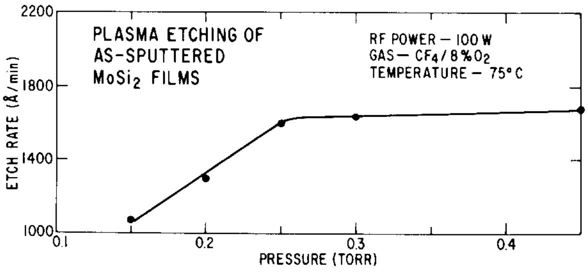

FIG. 3. Etch rate vs ambient pressure for as-sputtered $MoSi_2$ films.

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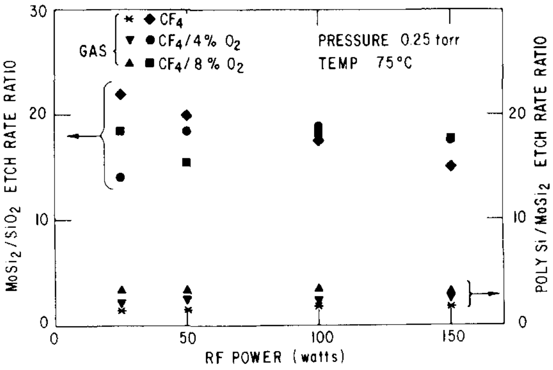

FIG. 4. Etch rate selectivity of $MoSi_2$ vs SiO_2 and $MoSi_2$ vs poly-Si as a function of rf power.

pear to have only a weak effect on the etch rate ratio. To evaluate the selectivity obtained, let us consider a typical VLSI circuit using a 3000-Å $MoSi_2$ electrode over 300-Å SiO_2 gate insulator. For a film thickness variation of $\pm 10\%$, the corresponding overetching required will result in etching approximately 30 Å of SiO_2 at 100 W of rf power. This represents only 10% of the gate insulator, an acceptable condition. It is interesting to point out that the $MoSi_2$ vs phosphorus-doped polycrystalline-Si plasma etching selectivity is between 2 and 3 (see the right-hand side of Fig. 4). Therefore this technique also appears to be useful in the one-step definition of "polycide" gates which consist[7] of a refractory metal silicide layer over a poly-Si underlayer. Reactive ion etching which has been used in the definition of the polycide structure[7] resulting in very abrupt side walls, suffers from low selectivity with respect to SiO_2 and thus requires a two-step etching process.

The etching process in a CF_4/O_2 plasma is attributed[4] to the free fluorine radicals formed by dissociative ionization of CF_4:

$$CF_4 \rightarrow CF_3 + F.$$

It is thought[5] that oxygen reacts with CF_3 radicals to further generate fluorine species and thus enhance the etching process. The basic reaction in the plasma etching of $MoSi_2$ is probably given by

$$MoSi_2 + 14F \rightarrow MoF_6 + 2SiF_4.$$

An exact identification of the reaction products must await mass spectrometric analysis. MoF_6 is a likely candidate because of its relatively high vapor pressure among fluorinated Mo compounds. The SiF_4 has been shown[5,6] to be the only Si–F compound resulting from the plasma etching of polycrystalline Si and SiO_2. If a relatively small percentage (4%) of O_2 is added to the CF_4 a near-linear etch rate–rf power relationship is observed [cf. Fig. 2(a)]. This indicates that the controlling factor in the reaction is the generation rate of free radicals, probably F^*. Doubling the O_2 concentration to 8% increases the etch rate substantially. However, at this high O_2 concentration, the etch rate saturates at a lower power level. This is probably due to the increasing importance of the surface reaction rate in determining the overall removal rate.

In summary, plasma etching of $MoSi_2$ films has been studied as a function of O_2 concentration, rf power, and pressure. Fine ($\gtrsim 1\ \mu m$) $MoSi_2$ lines over SiO_2 have been reproducibly obtained because of the high etch rate selectivity.

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[1] T. P. Chow and A. J. Steckl, Appl. Phys. Lett. **36**, 297 (1980).
[2] R. W. Kirk, in *Techniques and Applications of Plasma Chemistry*, edited by J. R. Hollahan and A. T. Bell (Wiley, New York, 1974), Chap. 9.
[3] A. R. Reinberg in *Proceedings, Symposium on Etching for Pattern Definition* (Electrochemical Society, Princeton, N. J., 1976), p. 91.
[4] C. M. Melliar-Smith and C. J. Mogab, in *Thin Film Processes*, edited by J. L. Vossen and W. Kern (Academic, New York 1978), Chap. V-2.
[5] C. J. Mogab, A. C. Adams, and D. C. Flamm, J. Appl. Phys. **49**, 3796 (1978).
[6] H. F. Winters, J. W. Coburn, and E. Kay, J. Appl. Phys. **48**, 4973 (1977).
[7] B. L. Crowder and S. Zirinsky, IEEE Trans. Electron. Devices **ED-26**, 369 (1979).

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