The large lattice constant observed in the region beyond 40% Sn is inexplicable. If tin atoms are incorporated as substitutional dopants, the lattice constant would be smaller than that of undoped sample because of the smaller size of Sn ions. One possible explanation is that tin atoms act as interstitial dopants, so that neighboring indium atoms are stretched apart due to the repulsion of the interstitial tin ions.

Conclusions

In this work, a simple evaporation process for producing ITO films was developed, namely, deposition by direct co-evaporation of metallic indium and tin. No indium tin oxide powder is required.

Under the following deposition conditions: (i) substrate temperature, 300°C; (ii) deposition rate, 20-40 Å/min; (iii) oxygen pressure, 1×10^{-4} torr; (iv) Sn/(Sn + In) weight ratio, 75%; and (v) film thickness, 1100Å; a good quality ITO film having the following properties was produced, *i.e.*: (i) sheet resistance, $15 \overline{\Omega/\Box}$; (*i*i) average transmittance, 90%; (*iii*) resistivity, $1.8 \times 10^{-4} \Omega$ -cm; (iv) mobility, $30 \text{ cm}^2/\text{V-2}$; and (v) carrier concentration, 1 $\times 10^{21}$ /cm³.

The improvement in resistivity results mainly from increasing the tin contents in the evaporation source, which is believed to be a doping process.

The major advantage of directly evaporating metal indium and tin over other methods (13, 14) is that no elaborate arrangement of In₂O₃ powder in evaporation source nor any expensive E-beam equipment is needed. The use of the Mo boat is better than the use of the crucible because it does not have the problem of spilling of In₂O₃ powder, blocking in the opening of the crucible by In_2O_3 powder, or cracking during high deposition rate. In addition, by controlling the amount of metal indium, the average deposition rate is so stable that no careful monitoring of deposition rate is required during deposition.

As a result, direct evaporation of metal indium and tin makes it attractive in most applications.

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Selective Molybdenum Deposition by LPCVD

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ABSTRACT

Molybdenum films have been deposited by low pressure chemical vapor deposition (LPCVD) on silicon substrates by the reduction of molybdenum hexafluoride in hydrogen and argon atmospheres. The deposition (Li CVD) on sincen substrates by with no Mo observed on silicon dioxide surfaces over the temperature range of 200°-400°C. Reduction by both hydrogen and silicon contribute to the deposition, with approximately equal, extremely high deposition rates; no self-limiting thickness was observed. Extensive TEM and SEM studies were conducted in order to characterize the microstructure of the deposited films. The main feature of the films is their extreme porosity—about 30%, which can explain many unusual proper-ties of the process and the films. On the basis of our experiments we propose a model to explain the origin of the porosity in the films. Comparative studies of tungsten and molybdenum LPCVD reveal that the difference between the two processes lie in the self-limiting mechanism occurring during the silicon reduction of tungsten hexafluoride.

LPCVD of W employing the fluoride chemistry has been a subject of study because of potential application of W to the needs of VLSI. Similar chemistry can be proposed for deposition of Mo from molybdenum hexafluoride MoF₆. The deposition of both metals is thought to evolve around two reactions

$$2MF_6(g) + 3Si(s) \rightarrow 2M(s) + 3SiF_4(g) \qquad [1]$$

$$MF_6(g) + 3H_2(g) \rightarrow M(s) + 6HF(g)$$
 [2]

where M stands for W or Mo, and s and g represent the solid and gas phases, respectively. The first reaction is the reduction of metal fluoride by silicon. Obviously, during formation of the metal layer some Si is consumed [about twice the volume of deposition metal (1)]. The second reaction is the reduction of metal fluoride by hydrogen. The free energy changes for these reactions are tabulated below (2):

| $T = 400^{\circ}\mathrm{C}$ | | Reduction by Si | Reduction by H_2 |
|-----------------------------|----|-----------------|--------------------|
| ΔG | w | -176 | -10 |
| (kcal/mol) | Mo | -213 | -50 |

These calculations indicate that reactions 1a and b are thermodynamically favorable and, therefore, a selective deposition process of Mo is possible in analogy to tungsten deposition. Also these calculations show that the driving force for the silicon and hydrogen reductions are greater for MoF₆ than for WF₆ and that reduction by silicon has a greater driving force than reduction by hydrogen.

The existing literature on the LPCVD of Mo is limited. In some studies molybdenum pentachloride was used as

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a source of Mo (3-5). Other authors have used molybdenum hexafluoride, but for metallurgical applications which require high deposition rates over large areas. Bulk Mo or other metals were used as substrate materials and experiments were carried out at high deposition temperatures and atmospheric pressures (6, 7). Few authors have considered LPCVD of molybdenum through MoF₆ reduction for integrated circuit applications. Schottky diodes were formed by the selective deposition of 800Å thick Mo layer in the temperature range of 200°-500°C (8) and Mo layers have been formed on patterned n^+ polysilicon lines (9). The temperature range of the deposition of this process was 390°-450°C and the process was reported to lose selectivity after the deposition of 0.3 μ m. Both works utilized only MoF₆ reduction by Si; no hydrogen reduction was reported.

In this study, the selective Mo LPCVD process was studied over the temperature range of 200°-400°C. Deposited films were extensively studied by scanning and transmission electron microscopy and by Auger, Rutherford backscattering, and x-ray photoelectron spectroscopies.

Experimental Procedure

The Mo films were deposited in a hot walled tubular reactor of in-house design shown schematically in Fig. 1. The reaction takes place in a quartz reaction tube that is 13 cm in diameter in a calibrated uniform temperature zone of 30 cm. The flow of gases was regulated by mass flow controllers and the reactant gases were of the following purity: argon 99.99%, hydrogen 99.99%, and molybdenum hexafluoride 99.9%.

The handling of MoF₆ and its reaction products proved more difficult than many other LPCVD chemistries. The reaction of MoF_6 with air (presumably moisture) forms a dark blue, highly viscous liquid that readily clogs mass flow controllers and drastically shortens pump life. The deleterious effect on the LPCVD equipment of the reactant by-products was far greater when using MoF₆ than for WF₆. Therefore, special precautions were taken to protect the parts of the system carrying MoF₆ from any exposure to the atmosphere. (In Fig. 1 these parts are enclosed within a broken line.) The system was equipped with two pumps. The process pump P_1 and the loading pump P_2 can be separated by a valve V_1 so that P_1 is never exposed to the air and P_2 never has contact with the reactant gas. The small tube furnace (afterburner) with Ta foil inserts was operated at 800°C to reduce the flow of reactant gas MoF_6 into P_1 . The base pressure in the reactor was 1.5 mtorr and the leak rate in the system was ≈ 0.3 mtorr/min. The depositions were made by flowing MoF₆ and either Ar or H₂. The pressure in the reactor was varied from 0.2 to 0.9 torr and the temperature from 175° to 400°C, with most experiments carried out at 0.2 torr and 250°C. The reactor was cooled to 150°C before venting to the atmosphere unless otherwise stated.

The substrates for deposition were of the following types: unpatterned Si wafers, Si wafers with patterned 1000Å thick SiO₂, and Si wafers with a 1 μ m deposited oxide layer patterned with 1.5 μ m windows. Prior to deposition, the substrates were cleaned in the mixture of H₂SO₄ and H₂O₂ and then immersed in 100:1 HF for 2 min, followed by a 5 min rinse in deionized water and a



Fig. 1. Schematic diagram of Mo LPCVD station



Fig. 2. Dependence of deposited Mo film thickness on time for different process conditions.

spin dry. Other films such as Al, TiN, W, Co, CoSi₂, and TaSi₂ deposited on Si were also used as substrates.

The thickness of deposited films was measured by SEM cross-sectioning and by using a beta-backscatter thickness measuring system¹ calibrated against Mo standards which were sputter deposited, chemically etched, and measured by surface profilometer.

Results

Deposition rates.—In Fig. 2 we plot film thickness vs. time for different process conditions. The film growth is extremely fast and linear with time. An interesting feature is the incubation time that precedes deposition. Probably this time is necessary for Mo nucleation on Si surface, and it is shorter for higher deposition temperatures and for hydrogen-containing reactant gas streams. Clearly the deposition rates strongly depend on temperature-the films formed at 250°C are an order of magnitude thicker than the films deposited at 200°C. The incubation time at 200°C is approximately 3 min, compared to 1 min at 250°C. It is also evident that the deposition rate depends on the ambient: in hydrogen the deposition rate is almost a factor of two higher than in the inert Ar atmosphere. This result implies that deposition in hydrogen is a sum of the two processes [1] and [2]. Comparing the deposition rates we can infer that both processes contribute approximately equally. This is quite different from the LPCVD of tungsten when the reduction by Si

¹ Micro-Derm MP-800, UPA Technology, Inc., Syosset, New York.



Fig. 3. Dependence of Mo film thickness on MoF₆ flow rates

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The deposition rates depend strongly on the availability of MoF_6 in the gas mixture. This dependence is plotted in Fig. 3 for two temperatures, 200° and 250°C. In these experiments the pressure, the flow of hydrogen, and the deposition time were kept constant while the MoF_6 flow was varied. For low flows, when the growth is limited by the availability of MoF_6 in the reactor, the thickness of the films is proportional to the flow rate. At high flows the growth is limited by the reaction rate and does not depend on the flow. Note, that at 250°C one can grow 7 μ m Mo film in only 15 min. At 200°C, the thickness obtained in the same time is 0.5 μ m. Even for the thickest films the process always preserves absolute selectivity; no deposition of Mo on SiO₂ was ever observed.

Deposition on substrates other than silicon.—We tested the process of Mo LPCVD on silicon substrates coated with different materials. These experiments were carried out in hydrogen at 250°C. The purpose of these experiments was to examine the interaction of the MoF_6/H_2 chemistry with substrates other than silicon and, in particular, to determine conditions for stopping the silicon reduction reaction by interposing a barrier layer. The MoF_6 flow was sustained at 10 cm³/min, and the duration of each deposition was 15 min. The deposition layers were studied by Auger spectroscopy. Results of the experiments are tabulated below:

| Coating material | Result | |
|-------------------------------------|---|--|
| LPCVD W, 1000Å | Consumes W, deposits Mo after Si sur- face is exposed. | |
| Sputtered Al, 1 µm | Does not deposit on Al, forms a thin layer of AlF_3 on surface. | |
| Sputtered TiN, 1000Å | Consumes TiN, deposits Mo on exposed Si surface. | |
| Sputtered Co, 400Å | Forms a brown peeling layer, possibly CoF ₃ . | |
| CoSi ₂ , 1200Å | Deposits Mo on top of CoSi ₂ by reacting with Si of CoSi ₂ . | |
| Sputtered TaSi ₂ , 5000Å | Does not deposit on TaSi ₂ , roughens the surface. | |
| Sputtered PtSi | Slowly consumes PtSi. | |

Note that only Al and $TaSi_2$ were able to withstand the reaction with MoF_6/H_2 ; however, no Mo deposition took place on these substrates. When silicon was available, as in $CoSi_2$, the Mo deposition continued without measurable change in rate. The MoF_6/H_2 reactants were able to completely destroy other films such as TiN and W.

Impurity content.—XPS and Auger spectroscopies revealed that all LPCVD Mo films contain large amounts of oxygen, though this amount depends on the temperature at which the reactor was opened to air, as shown in the table below;

| T air, ℃ | Oxygen, atom percent | |
|----------|----------------------|--|
| 25 | 4 | |
| 150 | 8-10 | |
| 250 | 20 | |

Apparently, the exposure of the films to air at higher temperatures causes the retention of oxygen to be greater. Oxygen was distributed uniformly through the thickness of the layer. This indicates that oxygen can diffuse freely through several microns of the film material. Even films exposed to air at 25° C contained unusually high amounts of oxygen (4%). No other impurities were found in the films.

Resistivity.—Resistivity of molybdenum films was obtained from sheet resistance and thickness measurements. The sheet resistance of Mo films was measured by the four-point probe method and the thickness of the samples was obtained from SEM cross-sectioning. Usually the films were cooled to 150°C before exposing them to air, and their resistivity was measured to be ~90 $\mu\Omega$ · cm, a factor of 15 higher than a bulk molybdenum. If the reactor was cooled to room temperature, the resistivity was found to be ~60 $\mu\Omega$ · cm, still an order of magnitude higher than in bulk Mo.



Fig. 4. SEM micrograph of a Mo film deposited on a flat Si substrate

Film Morphology

General.-Scanning electron micrographs (SEM) of typical LPCVD Mo films are shown in Fig. 4 and 5. The approximately 2 µm film in Fig. 4 was deposited on Si substrate. The Mo-Si interface is rough, indicating that Si reduction takes place. The film has an open, loose columnar morphology. Figures 5a and b show the structure of Mo films at the edge of a 1000Å thick SiO₂ pattern. The film in Fig. 5a was deposited in Ar atmosphere, so that no hydrogen reduction reaction could occur. The film in Fig. 5b was formed in H₂ atmosphere, so that both Si and H₂ reduction reactions contributed to the film growth. The most striking feature of these films is the extensive voids at the SiO₂ edge. These voids are a manifestation of the Si reduction reaction, in which deposited Mo occupies only half of the volume of displaced Si. As seen in Fig. 5a, away from the oxide pattern edge the Mo film



Fig. 5. SEM micrographs of the Mo films deposited on the SiO patterned Si substrate. (a) Deposition of MoF_6/Ar atmosphere; (b) deposition in MoF_6/H_2 atmosphere.

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Fig. 6. Planar TEM micrograph of a void at the edge with the ${\rm SiO}_2$ pattern.

surface is below the level of the original interface. The structure in Fig. 5b is produced by a deposition with both the hydrogen and the silicon reduction acting: hence the SiO_2 "marker" is embedded in the deposited film.

The microstructure of the voids at the edge of the SiO_2 pattern is seen in the planar TEM micrograph in Fig. 6. The Mo film in this picture is relatively thin (3000Å), so that the void is not extensive. The sponge-like Si surface is covered with short tunnels containing a Mo particle at the end of each tunnel.

The deposited structures shown in Fig. 7a, b also support the conclusion that two reactions take part in the deposition process. The contact window in Fig. 7a was exposed to the MoF_6/Ar atmosphere. A large volume of the Si substrate has been removed during the deposition of the mounds of Mo. The window in Fig. 7b was exposed to MoF_6/H_2 atmosphere. The substrate also shows voids similar to Fig. 7a, but the volume of deposited Mo is much greater, and the window is filled. The difference in total Mo volume is clearly due to H_2 reduction, while the similarity in the substrate erosion is the result of the Si displacement reaction.

In Fig. 8 a cross-sectional TEM micrograph depicting the structure of the Mo-Si interface is shown. One can see microscopic protrusions densely covering the interface. These protrusions contain small particles which are either metallic or metal-containing. Evidence for this comes from a high resolution TEM of the Mo-Si interface (Fig. 9) which clearly shows periodic lattice and moiréfringe patterns. Similar morphology has been reported to exist at the W-Si interface (10). The analysis of the electron diffraction pattern identified the particles as either Mo or MoSi₂. An even more remarkable similarity between Mo and W LPCVD processes is that the wormholes usually observed at the W-Si interface (1, 11) were also observed at the Mo-Si interface (Fig. 10).

Porosity of Mo films.—We have discussed some specific features of Mo films: extremely high deposition rates, uninterrupted Si reduction, uniform oxidation, and high



Fig. 7. SEM micrographs of 1 μm windows in PTEOS, subjected to Mo LPCVD process. (a) In MoF_6/Ar atmosphere. (b) in MoF_6/H_2 atmosphere.

resistivity of the films. All these properties can be readily understood by invoking the porosity of the films.

Quantitatively the porosity was determined by comparing the geometrical thickness of the film with the projected thickness of theoretically dense material. The geometric thickness was determined by SEM cross-sectioning, and the thickness of theoretically dense material was calculated from an RBS spectrum of the same sample, taking into account the oxygen content of the films. The ratio of bulk to geometric thickness was found to be



Fig. 8. Cross-sectional TEM micrograph of Mo-Si interface



Fig. 9. High magnification cross-sectional TEM micrograph of Mo-Si interface.

0.7, meaning that the density of the deposited films is only 0.7 of the density of bulk Mo. Such extremely high porosity of the films allows reactants and products to move freely to and from the silicon/metal interface, and can explain the unusual properties of the deposition process and the deposited film structure. In a random threedimensional two-phase structure the percolation of one phase occurs when it occupies more than approximately 25% of the volume (12) (percolation indicates a path through a continuous two-phase body lying entirely within one phase). This means that both phases can be mutually percolating if one phase occupies between 25 and 75% of the volume, a condition fulfilled in LPCVD Mo films in which bulk metal occupies 70% and voids occupy 30% of the bulk. Moreover, the incompletely randomized structure of the voids with vertical channels



Fig. 10. Cross-sectional TEM micrograph of Mo-Si interface showing the wormholes at the interface.

between the grains, as shown in Fig. 4, further facilitates percolation. This model can account for the uninterrupted reaction of Si with MoF_{σ} —both reactant and product gases can easily diffuse through the open porous structure. The porosity is also responsible for the uniform oxidation across the film thickness and the high resistivity of the films.



Fig. 11. Planar TEM micrograph of 2000Å thick Mo film. (a) 25,000 magnification. (b) 350,000 magnification.

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Strong evidence of the extreme porosity of Mo films is given in Fig. 11a, b. Here we show a TEM planar view of a 2000Å film. These micrographs were made using a 300 keV electron beam. The Si substrate under the Mo layer was thinned but remained intact. The Mo film was also protected from the top by sample mounting material so that the observed voids are not artifacts of sample preparation. In Fig. 11a one can distinguish small crystallites which collectively form into large loose clusters. These clusters are only locally connected and form large voids. The voids appear as long fissures in the microstructure, typically ~ 0.5 µm wide and several microns long. Higher resolution TEM (Fig. 11b) suggests that the porosity of smaller dimensions (<1000Å) is also present. One can distinguish in the figure small clusters less than 100Å in size which are loosely connected into larger clusters. In fact the film forms almost a fractal-like structure with porosity occurring at all scales. However, the presence of diffuse rings on the electron diffraction patterns (Fig. 11a insert) indicates that the film is polycrystalline. Most interestingly, similar porous texture was recently discovered in W films deposited by silicon reduction (13). Obviously the two processes have much in common.

The morphology of the films evolves during film growth, as illustrated by the SEM micrographs in Fig. 12. The surface of a very thin (≈ 100 Å) film is shown in Fig. 12a. One can distinctly see a dense network of fissures, similar to that shown in Fig. 11. The density of the fissures decreases and their scale increases as the film grows thicker (Fig. 12b, 0.2 µm). The surface of very thick films (Fig. 12c, 4 µm) looks absolutely smooth—all the fissures have disappeared. However, this does not slow down the further growth, indicating that the main transport of the reactant material occurs not through the fissures but through the smaller pores.

Discussion

The question of the origin of the porosity in the Mo films became especially challenging and problematic recently when similar texture was found in tungsten films deposited by Si reduction (13). In this section we propose a model for the formation of such porous texture, sup-



Fig. 12. Surface morphology of Mo films of different thicknesses



Fig. 13. Morphology of Mo films deposited with ${\sf SiF}_4$ in the reactive atmosphere.

ported by experiments in which silicon tetrafluoride SiF_4 was added to the reactive atmosphere.

Effect of silicon tetrafluoride SiF₄. Model for formation of porosity in Mo and W films.—The addition of SiF_4 to the reactant gases in W deposition was attempted in study (1) with the intent of minimizing Si erosion by shifting the chemical equilibrium of reaction [1]. The authors observed that the sheet resistance of deposited material increased with SiF₄ partial pressure and concluded that Si consumption was indeed suppressed. We carried out similar experiments in Mo deposition and observed a similar increase in sheet resistance. However we observed that while the SiF₄ curtails the Mo growth it does nothing to decrease the Si consumption. In Fig. 13 we show SEM cross sections of silicon wafers patterned with SiO₂ that were exposed to the reactant gases with SiF_4 added. It is obvious from the picture that the amount of deposited molybdenum depends on the SiF₄ flow-the higher the flow, the smaller the deposited volume. At some SiF₄ flows no metal is formed, but silicon is still consumed, as indicated by the craters formed in the Si substrate. It is clear that addition of SiF_4 does not prevent Si erosion, but it effectively prevents metal deposition. Interestingly, for complete Mo removal, the flow of SiF_4 should be a factor of two higher in the hydrogen/MoF₆ atmosphere than in the Ar/MoF₆ atmosphere. This is clearly due to the difference in the deposition rates in hydrogen and argon atmospheres (see Fig.

From our evidence, the mechanism of this effect is not clear. However, we can speculate that both W and Mo LPCVD are more complex than indicated by reactions [1] and [2]. Instead of [1] a generalized equation may be written

$$MF_n + SiF_m \rightarrow MF_{n-1} + SiF_{m+1}$$
 [3]

where *n* runs from 6 to 0 and *m* from 0 to 4. The intermediate reaction products may have very short lifetimes (only SiF₂, SiF₃, MoF₄, MoF₅, and WF₅ are known to be stable and volatile) but it may be sufficient to spatially and temporally separate the event of Si removal at M/Si interface (m changes from 0 to 1) from the event of M formation (*n* changes from 1 to 0). The addition of SiF_4 may affect one of the intermediate reactions leading to metal atom formation and hence decrease the M deposition rate, but still have no impact on the reaction of Si sublimation. Given this assumption the next step is to speculate that since SiF_4 is a final product of the Si reduction reaction, it is always present in the film during the process and may locally impede metal deposition causing porosity in both Mo and W. However, there is a significant difference between the two materials: whereas Mo has the same porous structure whether deposited in hydrogen or argon, W exhibits porosity only when deposited in an Ar atmosphere (13). This difference still requires further investigation although some factors can be pointed out: Mo has two lower fluorides, MoF₃ and MoF₄, which are both volatile and stable, while for W only WF₅ is known to have these properties; also, MoF₆ in H₂ atmosphere is known to etch metal Mo (7) which may result in fractional removal of Mo deposited by hydrogen reduction.

Comparison of the W and Mo LPCVD processes.—In this section we present a parallel analysis of the main features of the W and Mo LPCVD processes:

1. Deposition kinetics. Deposition of W by silicon reduction exhibits the self-limiting effect. This is different for Mo, where the deposition by both silicon and hydrogen reductions is linear with time.

2. Selectivity. Whereas the Mo LPCVD always yields selective deposits, the process for W is strictly selective only prior to the onset of the self-limiting mechanism, *i.e.*, during Si reduction.

3. Porosity. While Mo films are always porous, tungsten films are porous only when deposited by Si reduction.

4. Morphology of the metal-silicon interface. There is a striking similarity between the interfaces of both metals with silicon. Both interfaces are rough, with characteristic protrusions and wormholes.

The above observations led us to the following conclusion: the W deposition process is identical to the Mo process until the onset of the self-limiting mechanism for Si reduction whereupon only hydrogen reduction of WF_6 occurs, with dramatic changes in the texture of the films (large, densely packed grains). Before that moment, however, the two processes yield similarly porous selective deposits. The similarity of the interfaces with Si also suggests that in the beginning both processes run a very similar course.

Interestingly, under certain conditions the self-limiting mechanism in WF_6 reduction by silicon does not occur. Experiments with W CVD at atmospheric pressure in a nitrogen ambient yielded results very similar to Mo process: the growth of tungsten deposits is linear with time, the films are porous and the deposition is selective (14, 15). The disappearance of the self-limiting effect is not understood. However, it is clear that the processes of Mo and W CVD exhibit consistent similarities, while the difference in the kinetics and appearance of the films is entirely due to the self-limiting effect which occurs in the silicon reduction of WF_6 .

Conclusions

We have studied LPCVD of molybdenum on Si substrates using the reduction of MoF_6 . Two reactions contribute to the film growth: reduction by Si and reduction by H₂. We demonstrated that both reactions occur simultaneously at approximately equal, extremely high deposition rates. The film growth is proportional to the deposition time, and there is no self-limiting thickness at which either of the reactions stop. No nucleation of Mo was observed on SiO₂, even for the thickest films. The deposition rates depend on temperature, ambient, and MoF_6 flow.

The main feature of the deposits is their extreme porosity—about 30%. The films grow in a loose, open structure which is easily penetrated by the reactant gases. The porosity can explain such specifics of the process as the high deposition rates and the ever-continuing reaction of Si with the molybdenum reactants.

The deposited films have a resistivity which is an order of magnitude higher than that of the bulk molybdenum because of the extreme porosity of the films. The oxygen content in the films varies from 4 to 20%, depending on the temperature of exposure of the films to oxygen. No other impurities were found in the films.

The morphology of the films—rough interface, poor barrier properties, extensive voids—makes this process an unlikely candidate for existing contact metallization requirements. However, the results of the study are of considerable importance because they shed light on the nature of the widely used W CVD process. On the basis of our experiments in which SiF₄ was added to the reactive ambient we proposed a model explaining the porosity in both W and Mo films. We demonstrated that the difference between the two processes lies in the self-limiting mechanism of WF₆ reduction by Si, whose nature is not understood and poses a challenge for future research.

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