

Invited**Interface Reaction Control for Future ULSI Metallization Process**

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The precise control of interface reaction between adsorbate and solid surface will be the key issue for future thin film growth technology. The importance of electronic interactions for the selective thin film growth, such as molecule dissociation due to electron transfer from the substrate and the dipole attraction between polarized molecule and ionic material, has been demonstrated, considering examples of selective W and Cu film growth on Si and SiO₂, respectively.

1. Introduction

In the past ten years, dry etching technologies, employing a low pressure plasma, have been rapidly introduced into the VLSI production line, and they strongly promoted the shrinkage of minimum device feature size. ULSI manufacturing in the next decade, however, necessitates high quality, thin film growth technologies and especially, the selective growth techniques for various metals and insulators, which have the possibility to overcome several issues associated with submicron multilevel interconnection, would be the key to future ULSI devices.

In order to realize the highly selective thin film growth technique, it is very important to prepare a well controlled surface in situ and to control the interface reaction precisely. However, the mechanism study for the selective thin film growth is not sufficient for clarifying the elementary process and, up to date, there seems to be no useful guiding principle concerning the issue from which the selectivity in the film growth is derived. From the viewpoint of practical use, it is indispensable to clarify the origin of the selectivity, and to make some trials regarding new process and equipment, based on physics and chemistry.

This paper refers to the importance of electronic interaction between adsorbate and solid surface for the selective thin film growth, considering examples of selective W and Cu film growth employing WF₆ + SiH₄ and acetylacetonato copper complex, respectively.

2. Selectivity Control

2.1 Selective dissociation due to electron transfer

It is well known that W film grows on the Si surface by low pressure chemical vapor deposition, while it is not grown on SiO₂ ⁽¹⁾. Figure 1 shows the weight changes for W grown on the Si surface as a function of growing time ⁽²⁾. After W growth, the W deposited on the Si surface was all dissolved in the HCl + H₂O₂ solution, and the W weight gain was determined by means of inductively coupled plasma mass spectrometry (ICP MS) ⁽³⁾. In the case of WF₆ + SiH₄, first, the weight gain increased gradually with increasing the growing time, and suddenly, rose after a short induction time, of about 10 seconds. On the other hand, when WF₆ + Ar was used, the weight gain only continued to increase at the same rate as the initial growth rate for WF₆ + SiH₄. This result demonstrates that WF₆ was reduced by reaction with Si substrate at the initial stage, even if WF₆ + SiH₄ was used. For the selective W growth obtained by the WF₆ reduction due to reaction with the Si substrate, J.A. Yarmoff et al. made it clear that the dissociative chemisorption of WF₆ on Si is complete, even at room temperature, which results in the seed layer formation, and further W film growth is promoted by adding reducing agents, such as H₂ and SiH₄, to WF₆ ⁽⁴⁾. However, the mechanism for WF₆ dissociation on the Si surface still remains unclear.

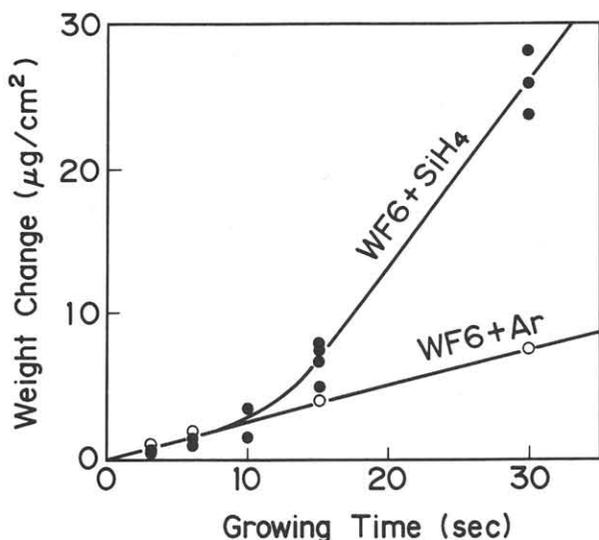


Fig. 1 Weight changes of W v.s. growing time

In order to obtain a useful insight about the initial stage in WF_6 dissociation, the W growth was carried out on several insulators, such as Al_2O_3 , Si_3N_4 , SiO_2 and LiF, employing $WF_6 + SiH_4$. Figure 2 shows an optical photograph of respective material surfaces observed in the dark field as a function of the electronegativity, which was defined as the arithmetic mean value of Mulliken's electronegativity for respective atoms constituting individual insulators (5). As the bond property of the substrate material becomes ionic, W growth is not easy. However, selectivity is inclined to be lost, when the growing time is prolonged. Taking these facts into account, the growing time was fixed at a relatively long 5 minutes.

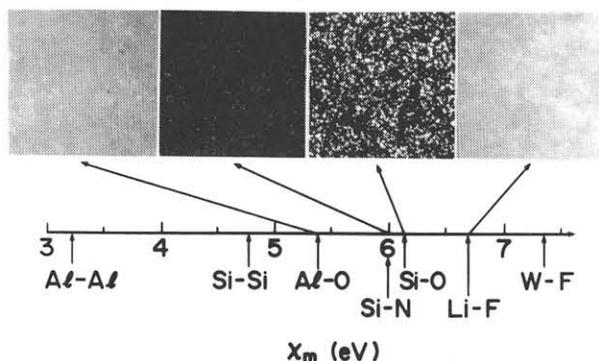


Fig. 2 Optical photographs of insulating film surface observed in the dark field

In the dark field observation, W islands were projected as bright spots on the photograph. From the result indicated in Figure 2, it was found that W film grew thick on Al_2O_3 surface, while W islands

only existed on both Si_3N_4 and SiO_2 surfaces. Furthermore, W island density on Si_3N_4 is much higher than that on SiO_2 . On the other hand, no W islands were formed on the LiF substrate. The above results can be summarized as indicating that WF_6 dissociation proceeds on the Al_2O_3 , Si_3N_4 , SiO_2 and LiF surfaces, in this order, reflecting the difference in average electronegativity. Considering the electronegativity concept, Figure 2 suggests that electron transfer from the substrate to adsorbed WF_6 molecule strongly enhances the dissociation.

In the down-stream selective etching of Si_3N_4 against SiO_2 , employing fluorine and chlorine atoms produced by a microwave discharge of $NF_3 + Cl_2$ gas (6), the possibility was demonstrated that the dissociation of adsorbed interhalogen molecules, such as FCl, which were generated from the gas phase titration reaction of fluorine atoms and chlorine molecules, is greatly enhanced by electron transfer from Si_3N_4 surface to adsorbed FCl molecule (7). Furthermore, it has been reported that Al film was selectively deposited on the Si surface by $AlH(CH_3)_2$ decomposition, due to electron transfer from Si to CH_3 group constituting source gas (8). The dissociation process for WF_6 on the Si surface seems to be basically similar to such a catalytic phenomenon.

Figure 3 shows the possible mechanism for WF_6 dissociation process, based on the average electronegativity concept. Since fluorine atoms, surrounding the centered W in the octahedral structure of WF_6 , have larger electronegativity, fluorine atoms pull the valence electrons from the Si substrate. As a result, relatively strong bondings between F and Si (96kcal/mol) are formed, accompanying the bond breaking for F and W (69kcal/mol), which results in the fluorine containing seed layer on the Si surface, and simultaneously releases the unsaturated molecules, such as $WF_{x(x=5)}$. The resultant WF_x molecules dissociated sequentially on the clean Si surface, due to the electron transfer controlled reaction. At present, the donation or backdonation level on the Si surface is not clear. However, according to this model, WF_6 dissociates readily on the n^+ Si surface rather than P^+ Si, because the n^+ Si substrate involved many free electrons near the surface. Actually, much of the n^+ Si substrate was consumed by the Si reduction of WF_6 , compared with the P^+ Si substrate, as shown in Fig. 4.

2.2 Selective adsorption through dipole attraction

Figure 5 shows a cross-sectional view of Cu film selectively grown on the SiO_2 lines employing bis-dipivaloyl methanato copper ($Cu(DPM)_2$) (9). The SiO_2 line and space pattern was formed by a wet chemical

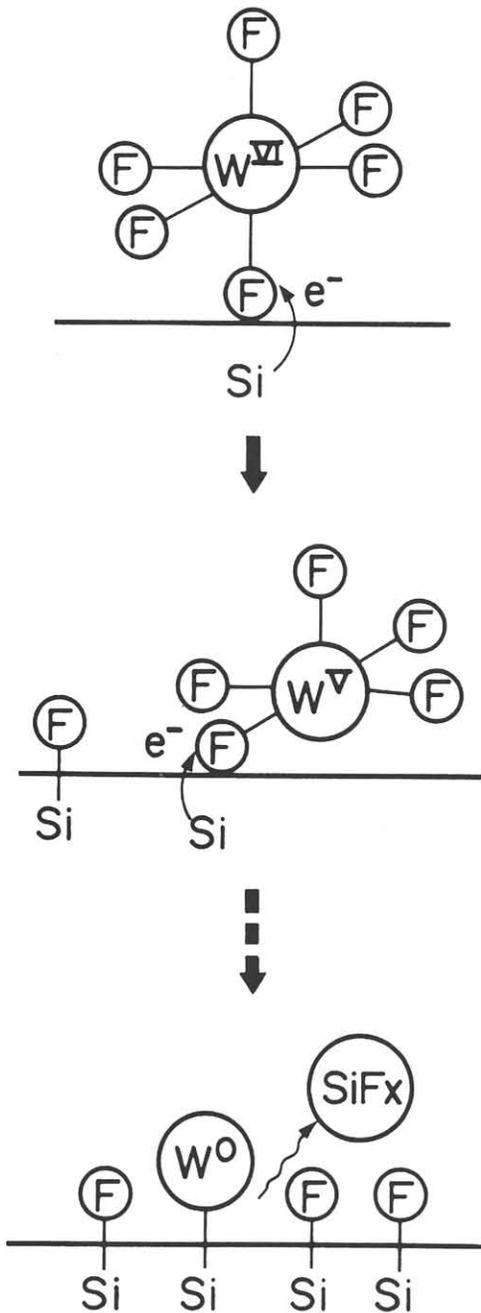


Fig. 3 Possible mechanism for WF_6 dissociation process due to electron transfer

etching of thermally grown SiO_2 film. The Cu film was inclined to be deposited selectively on the SiO_2 surface, but not on the Si substrate, when the vessel temperature went above about $100^\circ C$, regardless of the kind of acetylacetonato copper complex. Selectivity for the deposition, however, disappeared at relatively high vessel temperature, more than $300^\circ C$, and the Cu film grew on both SiO_2 and Si surfaces.

In order to clarify the mechanism for Cu film growth on the SiO_2 surface, the gas phase species, decomposed by heating the vessel, were analyzed by

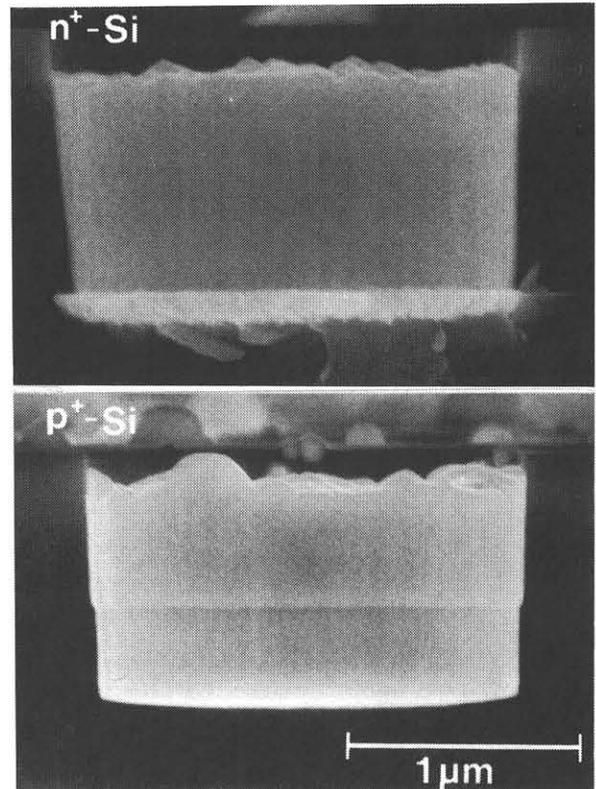


Fig. 4 Cross sectional view of W film selectively grown on the p^+ and n^+ Si substrates

the use of a quadrupole mass spectrometer. As a result, it was found that partially decomposed molecules, such as $CuC_4HO_2F_3$, $CuC_3O_2F_3$ and CuC_3HOF_3 , are present in the gas phase in the temperature range between 100 and $300^\circ C$. At present, details on the mechanism for preferential adsorption of these molecules are not clear. However, it can be conjectured that the strongly polarized molecules mentioned above condensed on the ionic SiO_2 surface, which led to the formation of a nucleation center for further Cu film growth, as shown in Fig. 6. On the other hand, these molecules do not adsorb on the Si surface with covalent bond. When the vessel temperature was raised to $300^\circ C$, the $CuC_4HO_2F_3$, $CuC_3O_3F_3$ and CuC_3HOF_3 molecules are further decomposed, and only stable products, such as $Cu(CO)_2$ and $CuCO$, remained in the gas phase. These molecules, whose dipole moments are extremely small, are considered to be adsorbed on both SiO_2 and Si surfaces indiscriminately.

Based on the mechanism for selective Cu deposition, the selective insulating film growth would be realized. Actually, it was confirmed that the silicon oxide film containing chlorine atoms was preferentially formed on the cooled SiO_2 surface, due to coulomb interaction between unsaturated silicon chloride compounds and ionic SiO_2 surface ⁽¹⁰⁾.

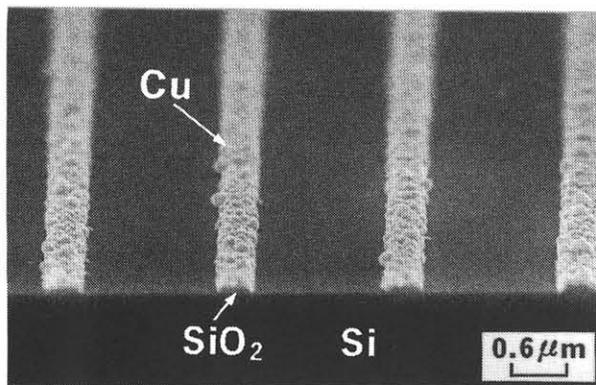


Fig. 5 Cross-sectional view of Cu film selectively deposited on the SiO₂ lines

3. Conclusion

Considering the reaction mechanism for selective W and Cu film growth on Si and SiO₂ surfaces, respectively, one of the useful guiding principles for selective growth procedure of metals and insulators has been proposed. More precise understanding of the interface reaction leads to the construction of a universal rule for the selective thin film growth. In the future, deep insight into the selectivity origin should be put to practical use, such as precursor design, surface modification and so on.

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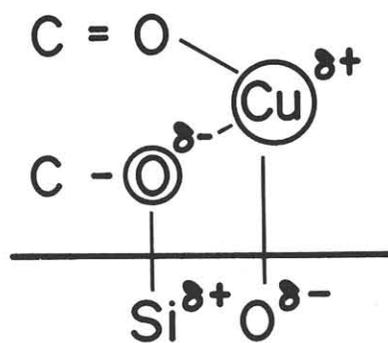


Fig. 6 Possible mechanism for selective Cu film deposition

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