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Growth Mode of Tungsten Thin Film by Using SiH_4 Reduction of WF_6 in LPCVD System

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저압 화학 기상 증착 조건에서 SiH_4, WF_6 환원 반응에 의한 텅스텐 박막의 성장 양식

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ABSTRACT

Tungsten thin film was deposited on Si(100) substrate by either Si substrate reduction of WF_6(case 1) or SiH_4 reduction of WF_6(case 2) in LPCVD system. The morphology and properties of deposited films for both cases were examined. The crystal structure for both cases was determined to be bcc (body centered cubic). The amount of tungsten and the grain size in thin films were increased as the film grows. From the experimental results and theoretical considerations, it can be understood that the tungsten thin film grows by the volmer-weber growth mode, that is, island growth. The detailed tungsten thin film growth mode is presented. It was also found that the initial polycrystal structure of tungsten thin film developed into single crystal structure as the film grew in thickness.

요 약

LPCVD 조건하에서 Si 기판을 이용하여 WF_6를 환원시키거나 SiH_4를 이용하여 WF_6를 환원시켜 Si(100) 기판위에 텅스텐 박막을 증착하였다. 증착된 박막들의 표면 및 단면 형상과 특성들을 조사하였으며 박막들의 결정구조는 체심입방구조를 이루는 α-W임을 알 수 있었다. 박막내의 텅스텐의 양과 grain들의 크기는 박막이 성장함에 따라 증가하였다. 실험적인 결과와 이론적인 고찰들로부터 텅스텐 박막은 Volmer-Weber 성장양식인 island growth를 이룸을 알 수 있었고 세부적인 박막 성장 양식을 제시하였다. 또한 텅스텐 박막이 성장할수록 박막의 결정구조는 점점 단결정화 하여감을 알 수 있었다.

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1. INTRODUCTION

Refractory metals, such as tungsten and molybedenum, and their silicides, such as WSi_2 and $MoSi_2$, have been regarded as good candidates to replace aluminum[1-4]. These materials have high melting point, high resistance against electromigration, and low electrical resistivity[5-6]. Among these materials, tungsten is of particular interest because it has a similar thermal expansion coefficient with silicon[7]. Moreover, it is known to have deposition selectivity, that is, it is deposited only on silicon surface[8]. So it has the cut off advantage the masking step in semiconductor processes. For the thin film deposition, PVD (physical vapor deposition) and CVD(chemical vapor deposition) methods have been generally used[9-10]. Among many variations of these techniques, the CVD technique, especially in the form of LPCVD(low pressure CVD), has shown much promise in tungsten thin film deposition, in particular for growth rate, step coverage and stress[11-13].

The study on the tungsten thin film deposition is classified into selective tungsten deposition utilizing the selectivity of tungsten deposition only on silicon(and not on silicon oxide) and blanket tungsten deposition experiment[8]. In selective tungsten deposition the deposition reaction is proceeded via reduction of tungsten source gas by Si substrate, so it frequently has the problem that tungsten intrudes into substrate which is placed below silicon oxide film, a phenomenon called encroachment[7-8]. Encroachment can corrupt gates and contact layers. In blanket tungsten deposition the deposition reaction is proceeded via reduction steps of source gases(WF_6, WCl_6, ··· etc.) by reducing gases(SiH_4, H_2, ··· etc.). The deposited tungsten thin film requires good compatibility with silicon substrate, high degree of uniformity and crystallinity, good electrical conductivity, and so forth. In both cases knowledge of the thin film growth mode is necessary to improve selectivity or characteristics of the resulting tungsten thin film.

Thin film growth mode is generally classified into Frank-Vander Merwe(FV) mode, Volmer-Weber(VW) mode, and Stranski-Krastanov (SK) mode, which represents respectively layer by layer, island by island, and layer plus island growth[14-16]. In VW and SK modes thin film grows by island formation, so the investigation on island formation is necessary for detailed understanding of the mode for thin film growth. In tungsten CVD WF_6 is usually used as a tungsten source gas, [17] while, SiH_4, with the advantage of compatibility with silicon substrate, and H_2 are used as reducing gases[18-19].

In this work we deposited tungsten thin films on silicon substrate using WF_6 as a tungsten source gas and SiH_4 as a reducing gas. We used LPCVD deposition technique to improve characteristics of the resulting tungsten thin film and deposited tungsten thin films with and without using reducing gas. The physical and electrical properties were investigated. From the obtained experimental results and theoretical considerations, a detailed growth mode for tungsten thin film was suggested.

2. EXPERIMENTAL

The LPCVD system of cold-wall type is shown in Fig. 1. The reactor wall was water-cooled. The temperature of the resistance heater

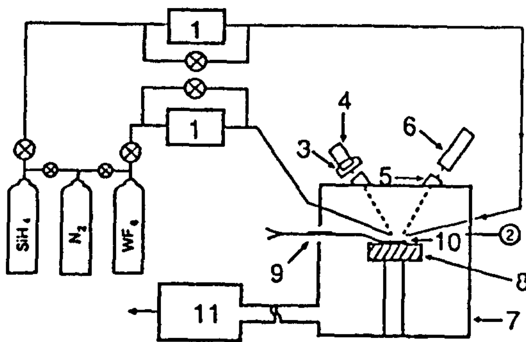

Fig. 1. Schematic diagram of LPCVD system.

was uniformly controlled during the reaction using the front side K type thermocouple (Chromel-Alumel) and a temperature controller (Omega 4001 KC). WF_6(99.999%, Takachiho) and SiH_4(99.999%, Takachiho) was used without further purification. Flow rates of WF_6 and SiH_4 were controlled by MFC(mass flow controller, Edward model 1605). Reactant gases were introduced through different inlet ports and mixed only on substrate. The total pressure in the reactor was maintained constant by using the adjustable outlet valve. A 100-mm diameter P-(100) Si wafer was used, following pretreatment with 10% HF buffer solution for 1min., then drying with nitrogen gas.

Film surface and cross section were examined by SEM(scanning electron microscopy, Jeol JSM840) and TEM(transmission electron microscopy, Hitachi H9000, 300KV). Composition of the film was determined by EDX(energy dispersive X-ray microanalysis) and AES(Auger electron spectroscopy, Perkin-Elmer PHI 610). Crystal structure was deduced from XRD(X-ray diffraction, Jeol DX-GD-2, Cu$k\alpha$-Ni filtered: $\lambda=1.5418$Å) spectrum and SAED (selected area electron diffraction) patterns from TEM. Film Thickness and electrical resistivity was respectively measured by Dektak and four point probe.

3. RESULTS AND DISCUSSION

We deposited tungsten thin film using different source gases (case 1 : WF_6 only; case 2 : WF_6+SiH_4 mixture) as listed in Table 1. From the AES depth profile(Fig. 2) and EDX spectrum(Fig. 3) of each case, we could estimate that the ratio of the deposited tungsten and silicon is similar for both cases. We determined the crystal structure of tungsten thin films by using XRD. Fig. 4 shows the X-ray diffraction spectra showing a strong intensity at W(110), and weak intensities at W(200) and W(211) positions for both cases. The XRD spectra indicate that the deposited film is mostly constituted by α-W which was bcc(body centered cubic) structure[20, 21]. As represented in Table 2, the

Table 1. Experimental conditions in LPCVD reaction

conditions/case	1	2
Source gas	WF_6+SiH_4	WF_6
Flow rate(sccm)	WF_6(36), SiH_4(18)	36
Reacton Temp.(℃)	450	450
Total pressure(mTorr)	250	150
Reacton time(min.)	30	30

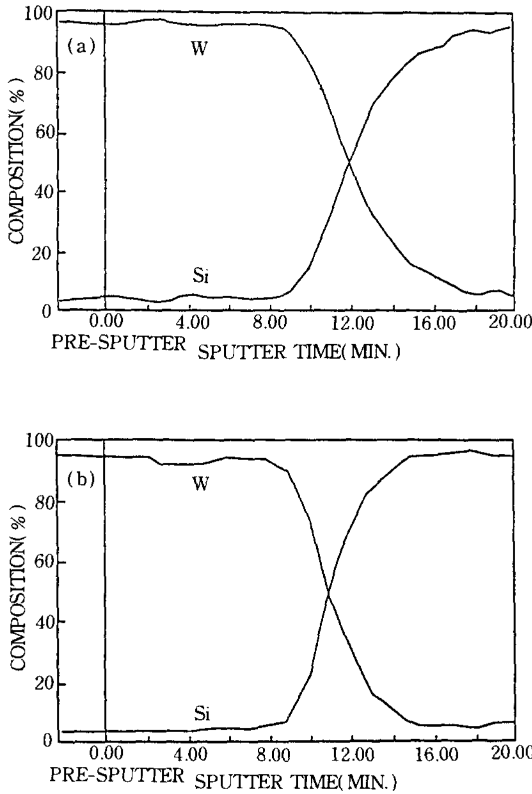

Fig. 2. AES depth profile for (a) case 1(WF_6 only condition) and (b) case 2(WF_6+SiH_4 mixture condition).

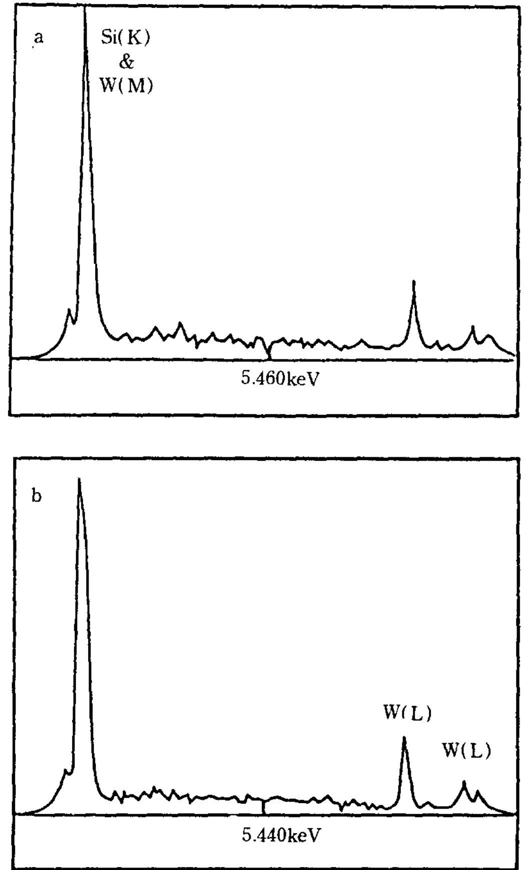

Fig. 3. EDX spectrum for each case of Fig. 2.

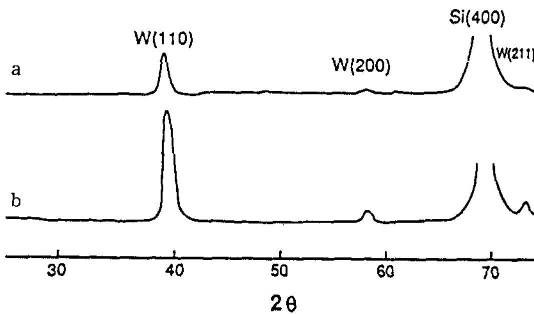

Fig. 4. XRD spectra for each case of Fig. 2.

film growth was limited to about 300 Å when only WF_6 was used, but when SiH_4+WF_6 mixture was used the film was grown to about 1 ㎛ within the reaction time of 30 minutes. The electrical resistivity values, also shown in Table 2, are constant (about 15 $\mu\Omega$-cm) in any case. This value is different from that(5.3$\mu\Omega$-cm) of bulk tungsten, the difference being due to grain boundary scattering of charge carriers as reported by Sivaram[22]. The surface was smoother when only WF_6 was used as a source gas. Fig. 5a shows cross sectional SEM micro-

Table 2. Film thickness, surface roughness and electrical resistivity

Experimental Conditions	Reactant gases	Thickness (μm)	Surface Roughness (arb. units)	Resistivity ($\mu\Omega$-cm)
Case 1	WF_6	~ 0.03	30	14.5
Case 2	WF_6, SiH_4	~ 1	10	15

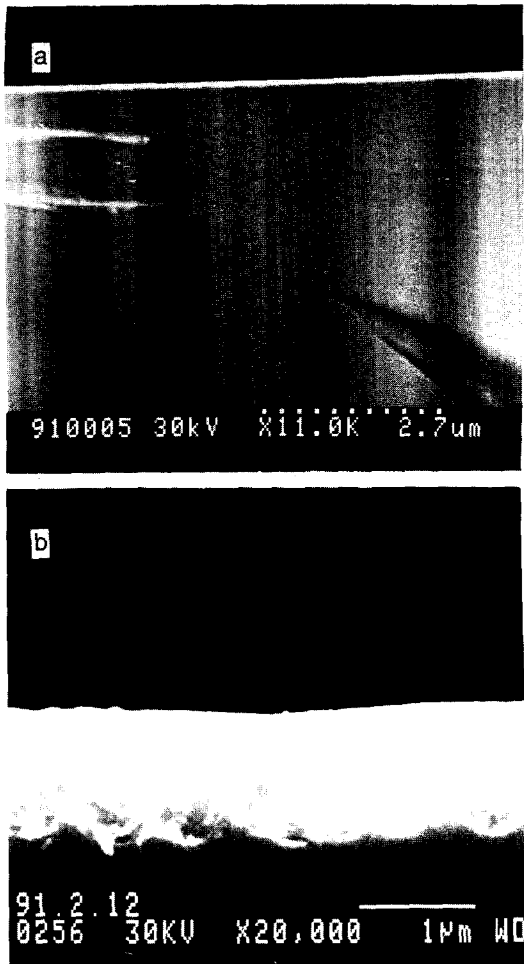

Fig. 5. Cross sectional SEM micrographs of thin film : (a) Si substrate reduction of WF_6, (b) SiH_4 reduction of WF_6.

graph of tungsten thin film when using only WF_6 source gas, which shows the self-limited thin film growth. This phenomenon, reported by many workers[20, 23], is understood to be due to the lack of active silicon species at the end of initial deposition. When only WF_6 was used as a source gas, the film surface was composed of small grains and pores[24] as shown in Fig. 6a. Fig. 6b shows the surface SEM micrograph taken 3 min. after the beginning of SiH_4 reduction reaction of WF_6(case 2). In this case very fine surface image was seen instead of porosity. When using WF_6+SiH_4 as source gases, the film surface shows a compact patterns of grains as shown in Fig. 6c. Grain sizes are measured to be about a few hundred nm. We investigated the sputter crater by SEM and found the pillar structure, also reported by Sivaram[22], as shown in Fig. 6d. This image reveals that the deposited tungstens are partly aggregated. The AES survey and X-ray mapping results of the tungsten thin film cross section were shown in Fig. 7 and Fig. 8. Unfortunately, in the latter case the tungsten M line overlaps with silicon K line in EDX. Therefore the X-ray mapping was carried out by selecting only the tungsten L line to determine the relative tungsten concentration. These figures show a higher tungsten intensity relative to silicon at regions farther away from the substrate. Actually, no Si Auger

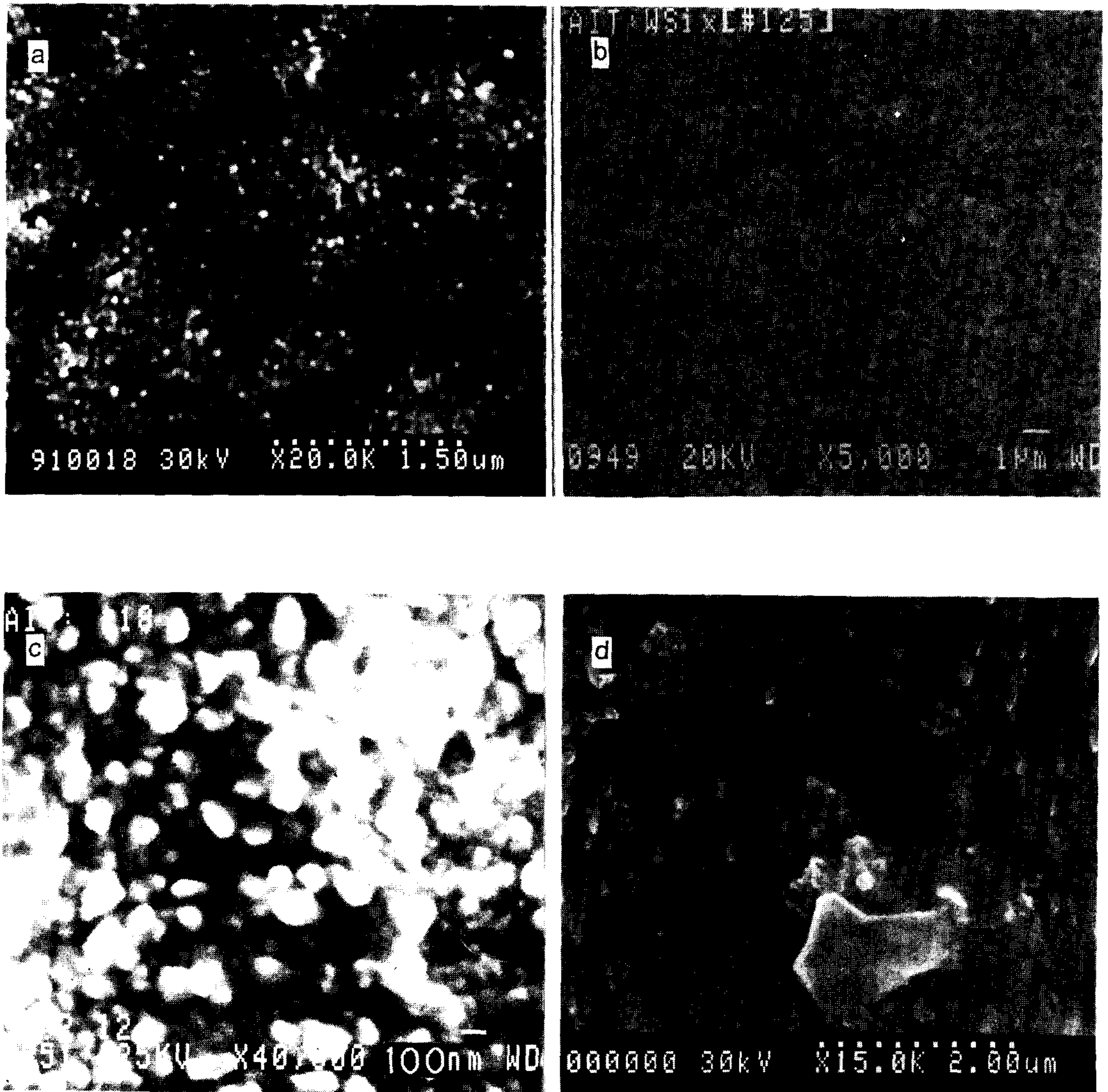

Fig. 6. SEM micrographs (a) thin film surface after 30 min. reaction for case 1, (b) thin film surface after 3 min. reaction for case 2, (c) thin film surface after 30 min. reaction for case 2, (d) the sputter crater produced during AES depth profile.

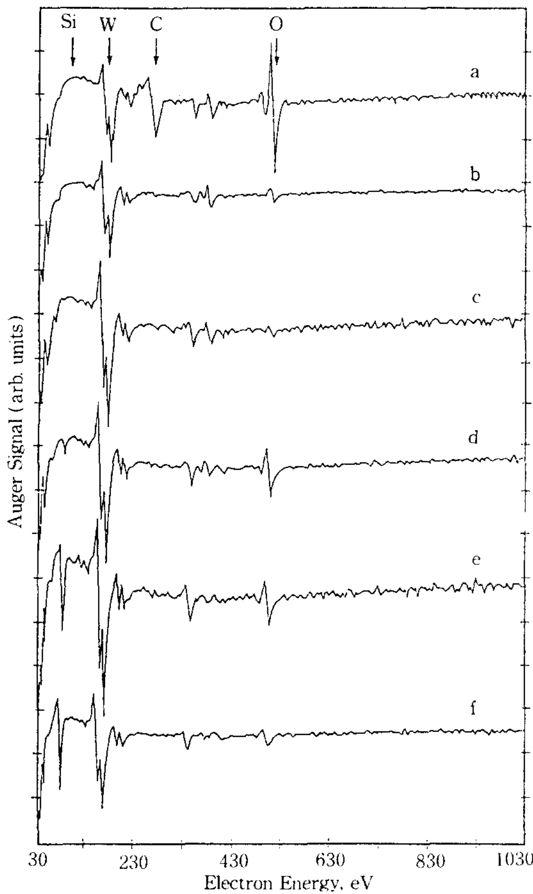

Fig. 7. Auger spectra of deposited tungsten thin film for case 2
(a) deposited tungsten thin film surface,
(b) after 1 min. sputtering,
(c) after 10 min. sputtering,
(d) after 40 min. sputtering,
(e) after 50 min. sputtering,
(f) after 60 min. sputtering.

signal was detected at the farthest layer from Si substrate. Fig. 9 shows the tungsten film cross sectional SAED pattern from TEM. From the pseudo-ring pattern of SAED, it is believed that thin film has a partially polycrystalline structure. This indicates that the tungsten thin film is grown by the island growth rather than by the layer-by-layer growth, which tends to show single crystal morphology.

From these results, detailed growth mechanism of tungsten thin film can be proposed by adoption of the nucleation theory[25] as follows. Tungsten atoms, which are produced by Si substrate reduction of WF_6, deposit on Si substrate and form the initial deposition nuclei by incorporating more adsorbed tungsten atoms which come into contact with the initial nucleus by surface diffusion. They soon assume the role as tungsten "pseudo-substrate". In this stage small grains and pores are shown in thin film surface as shown in Fig. 6a. After this stage, new tungsten nuclei are produced by SiH_4 reduction of WF_6. Smaller critical nuclei are formed at binding sites evidenced by the very

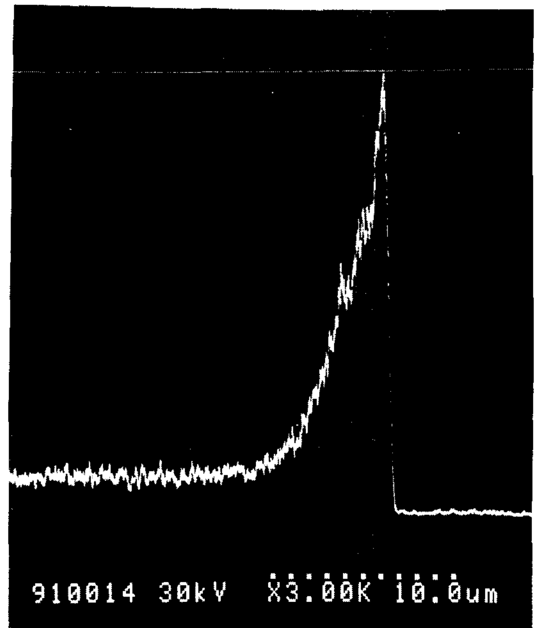

Fig. 8. Cross sectional X-ray mapping image of the tungsten thin film.

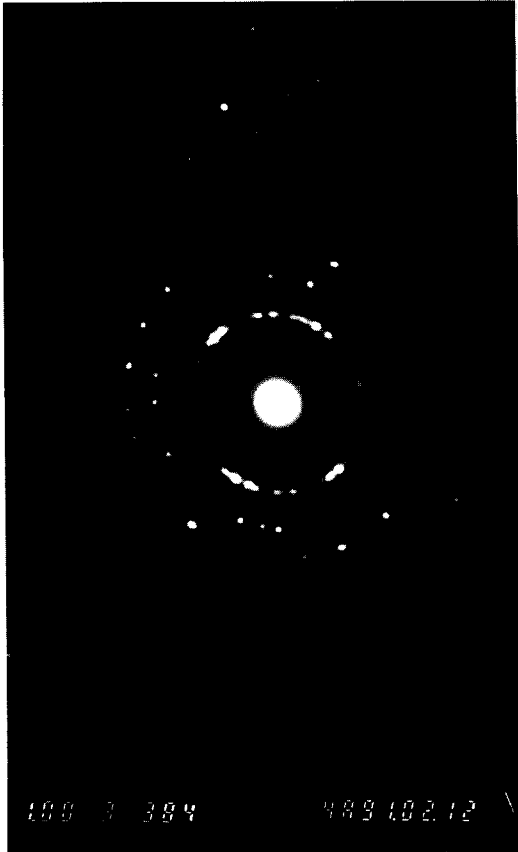

Fig. 9. Corss sectional SAED pattern from TEM for tungsten thin film.

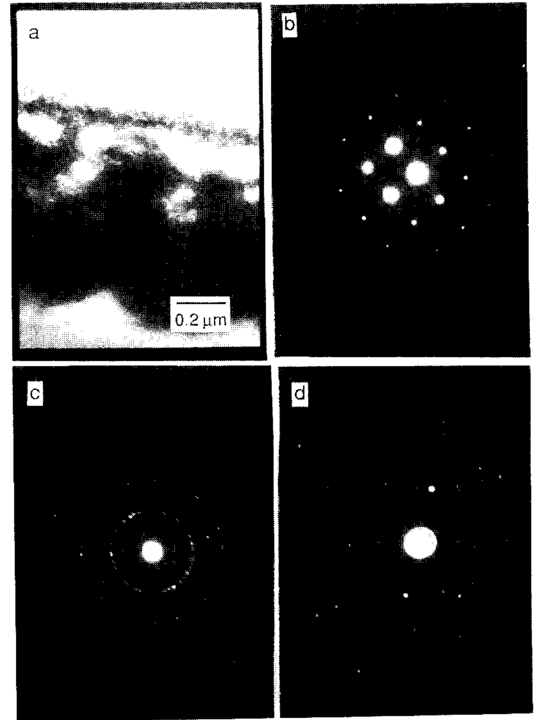

Fig. 10. (a) TEM micrograph of thin film cross section in the case of SiH_4 reduction of WF_6.
(b) SAED pattern of Si substrate.
(c) SAED pattern of thin film close to the Si substrate.
(d) SAED pattern of the thin film farther away from the Si substrate.

fine surface image shown in Fig. 6b. As the tungsten atoms are produced more by SiH_4 reduction of WF_6, they can move on tungsten nuclei by the surface diffusion motion. The binding energy between tungsten substrate and tungsten atom is reported to be 5.83 eV[26]. This value is regarded as sufficient for tungsten atoms to form clusters when they meet on tungsten substrate by surface diffusion. Because of the high binding energy between tungsten substrate and tungsten atom, they can form tungsten cluster. Like this, cluster meet another cluster and they coalesce together. Therefore their size increased and as a result they can form island. As the reaction proceeds the tungsten islands coalese together, which increase the size of island, and new islands are also formed at binding sites. In this way, the size of tungsten island grows in parallel with the growth of tungsten film thickness. Therefore very com-

pact and large size grains would be observed at tungsten film surface as shown in Fig. 6c.

We tried to investigated the crystal structure of thin film by SAED pattern from TEM. Fig. 10a shows TEM micrograph of thin film cross section in the case of SiH_4 reduction of WF_6. Fig. 10b, c, and d show respectively the SAED patterns of Si substrate, tungsten thin film closer to the Si substrate, and tungsten thin film farther away from substrate. In the SAED pattern of tungsten thin film a ring pattern is observed, which indicates that tungsten thin film has a polycrystalline character. But the comparison of Fig. 10c and Fig. 10d shows that the ring pattern of SAED is later changed to the dot pattern, which indicates that the initial polycrystal structure of tungsten thin film develops into single crystal sructure as film grows in thickness.

4. CONCLUSIONS

In the present work the density of incorporated tungsten was found to increase as the thin film grows in thickness. The size of tungsten island is also found to increase as the thin film grows. The following steps are proposed for tungsten film growth mode.

Step 1. Tungsten nucleus is produced on Si substrate by Si substrate reduction of WF_6.

Step 2. More tungsten atoms are produced by SiH_4 reduction of WF_6. They form tungsten cluster by surface diffusion.

Step 3. Cluster meet another cluster and they coalesce together. Therefore their size increased and as a result they can form island.

Step 4. Thin film grows as the size of tungsten islands grows.

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