Influence of external stress for non-equilibrium thin films.

N.Fujimura S.Tachibana* and T.Ito

Metallurgical Engineering, College of Engineering
University of Osaka Prefecture
Mozu-Umemachi, Sakai, Osaka 591 Japan
*Graduate school; University of Osaka Prefecture

INTRODUCTION

The structural controlling of bulk materials is widely industrialized. The grain size, the texture and the precipitation are perfectly controlled, which results in various preferable properties. While, in thin film materials, the non-equilibrium; that is to say, wide solubility limit; makes it complicated. For instance, in the case of Al-Si films used as a contact metal for Si devices, silicon dissolves in as-deposited aluminum more than solubility limit. During sintering, however, Si precipitates to the interface between silicon and aluminum, so-called Si precipitation. Moreover, we already reported that in Ti-rich TiNx/Si system, excess Ti reacted with Si substrate(1), and that in Si-rich WSix/Si system, excess Si precipitated at the film/substrate interface(2,3). If there are no driving forces, excess atoms are to precipitate in the film (grain-boundary). What is the driving force? How is the structure of films controlled? Our final aims are to make these points clear. As one of the methods to control the structure of the films, we paid attention to the influence of stress. The structural changes were evaluated under external stresses.

EXPERIMENTS

The $WSi_{2.6}$ films were deposited by a plasma CVD system dilectly on P type (100)Si substrate. WF_6 and SiH_4 were used as reaction gases, and these flow rates were 2 and 120 cm^3/min, Helium was used as a dilution gas. The pressure was 40 Pa. The substrate temperature was 350 °C. The film compositon evaluated by Rutherford backscattering was $WSi_{2.6}$. The prepared samples were annealed in a vacuum of 10^{-7} Torr. The structural change and the depth profile of the film composition were evaluated by X-ray and electron diffraction, and X-ray photoelectron spectroscopy(XPS).

RESULTS AND DISCUSSION

The structure of as-deposited sample is amorphous, and it crystallizes to a hexagonal WSi_2 by annealing at 400 °C for 1 h in a vacuum. It is observed by XPS that the excess Si has precipitated at the WSi_2 /Si substrate interface(Fig.1). As the WSi film is deposited by CVD, it is considered that the internal film stress in as-deposited state is induced by the difference between the thermal expansion coefficient of the film and that of the substrate when the samples are cooled from 350 °C(substrate temperature on deposition) to room temperature, that is, there is little influence by the intrinsic stress. The structural change can be observed without the influence of the film stress by annealing at 350 °C. However, about 29 Å of precipitation of excess Si at the interface was observed (Fig.1). This fact suggests that another mechanism (maybe a relaxation of

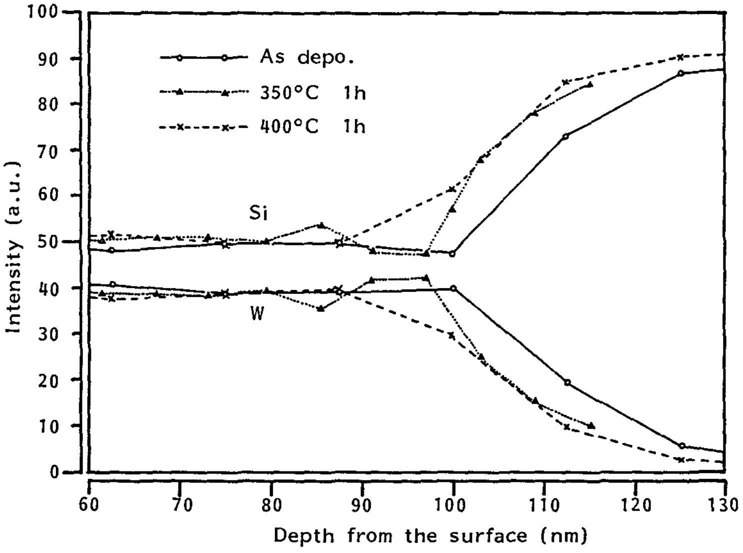


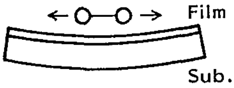
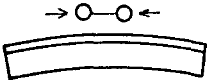
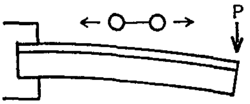
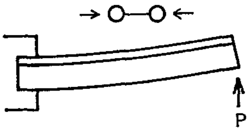
Fig.1 XPS depth profiles of the sample annealed at each temperature.

interfacial energy) is operating except film stress. If the film stress is concerned with the structural change, the process of the crystallization and the precipitation will be affected by applying larger elastic energy induced by the film stress than the interfacial energy.

To make clear the origin of the structural changes, the annealing samples under strong external film stress was performed. To discuss the results, it is necessary to describe about the difference between a concept of external stress and that of internal one.

To apply the external stress, the substrate, in a rectangular is clamped at the one side for the loading which is the constant displacement at another side (cantilever). In this case, the state of stress should be as in Table, by defining the elastic strain in the lattice of the film in contrast to the internal stress.

Table A concept of the stress.

	Tensile stress	Compressive stress
Internal stress		
External stress		

Since this external stress can be treated as the bending of cantilever, the stress is expressed as a linear function against the distance from the loading side, X,. Then, the external stress was obtained by calculating the radius of curvature at micro-distance (R Δx) and substituting it in Eq.(2).

$$\sigma = \frac{Ef}{6(1-\nu f)} \cdot \frac{ts^2}{tf} \cdot \frac{1}{R\Delta x} \qquad \text{Eq.(2)}$$

,where Ef, νf and tf are the Young's modulus, Poisson's ratio and thickness of the film, respectively. And, ts is the thickness of the substrate.

In this study, the value of Ef/(1-νf) was roughly estimated by assuming that the internal film stress in as-deposited state was induced by only the difference in thermal expansion coefficients.

Figure 2 shows the influence of external stress on the crystallization. By annealing at 350 °C for 1 h, samples with a external compressive stress (8.45×10^{11} dyne/cm^2) and without the external stress (maybe also without an internal stress at 350 °C) have not crystallized. While, those with an external tensile stress (1.13×10^{12} dyne/cm^2) have crystallized.

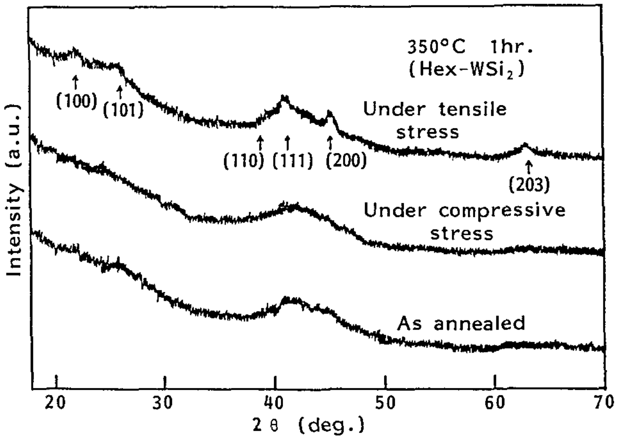


Fig. 2 X-ray diffraction patterns of each sample annealed at 350 °C.

The crystallization under the external tensile stress is caused by the enhanced diffusibility of atoms due to the expanding of the bonding. That is, it is considered that the external tensile stress is relieved by the crystallization(accommodation mechanism). Under the external compressive one, as the bonding is shrunk, the diffusion of atoms is suppressed and the crystallization is retarded.

Figure 3 shows the influence of external stress on the precipitation

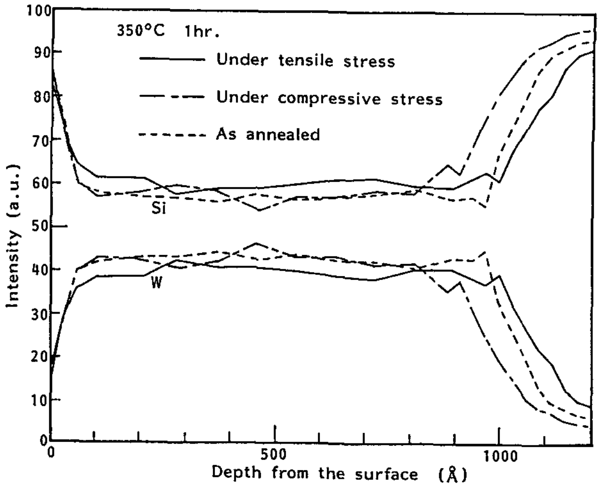


Fig.3 Depth profiles of XPS spectrum.

at the interface which is evaluated by XPS depth profile. The precipitation at the film/substrate interface resulted in the volume change of the film. The volume per unit of amorphous $WSi_{2.6}$ (initial state) was obtained by calculating the film density. The film density was calculated using Lorentz-Lorenz equation by measuring the refractive indices of amorphous $WSi_{2.6}$ and crystallized WSi_2 using ellipsometry. The volume of WSi_2 +0.6Si (precipitated in the film) and WSi_2 (precipitated at the interface) were calculated using their lattice parameters. These calculations indicates that if the precipitation of excess Si occurs in the film, the volume of the film hardly changes. But, the precipitation at the interface makes the film contract about 9.82 Å^3/molecular.

The compressive stress can be relieved by precipitation at the interface due to the volume decrement of the film. Therefore, the 88 Å of precipitation at the interface was observed under the external compressive stress(accommodation mechanism). The precipitation at the interface in the sample without stresses is considered to relieve the interfacial energy as mentioned above. On the other hand, under larger elastic energy induced by external tensile stress than the interfacial energy, the precipitation has not occurred, since the precipitation at the interface can make the elastic energy decrease in the film due to the volume decrement.

The obvious structural change of Si-rich $WSi_{2.6}$ was observed under the external film stress. When the interfacial energy between the film and the substrate is larger than the elastic energy induced by the film stress, the structure of the film changes to relieve the interfacial energy. In the contrary case, the structure changes to relieve the elastic energy induced by the film stress. In conclusion, the accommodation mechanisms on the structures are operating in the films to relieve a energy induced in the films.

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