EFFECTS OF SUBSTRATE COATING WITH METAL SPRAYING ON RESIDUAL STRESSES IN SPUTTERED TITANIUM-NITRIDE FILMS

* The University of Shiga Prefecture, Hassaka-cho, Hikone 522-8533, JAPAN
** NEOS Co.Ltd., Oikemachi, Kousei-cho, Kouka 520-3213, JAPAN

ABSTRACT

A fundamental study on the effect that pre-coating a substrate with metal spraying has on the properties of sputtered Titanium-nitride film (TiN film) was carried out. The residual stresses in TiN films sputtered on the substrates coated with various spray coatings were measured by X-ray stress measurement. It was observed that the residual stresses in TiN films sputtered on substrates coated by metal spraying were lower than those on the substrates not so coated. The influence of the surface configuration of spray coating on the residual stress in sputtered TiN film was also investigated. It was found that the surface configuration of spray coating affected the residual stress in TiN film, and that the residual stress increased with the surface roughness of the spray coating increasing.

1 INTRODUCTION

Today, “sputtering” is indispensable in the manufacture of semiconductor devices. However, as a by-product of the sputtering coating process, deposits are formed on the surface of the shutter plate, shield, and so on. The thickness of the deposit increases with operating time, and at last, a great number of particles generate from the deposit. Currently, the particle generation is recognized as one of the most serious problems in the manufacture of semiconductor devices [1]-[6]. This is because these particles make the ratio of defective products so high by attaching to the products. As one of the countermeasures against the particle problem, the shutter plate etc. are often coated by metal spraying before such the deposits are formed. This method is effective in decreasing the number of the particles, and is widely used in Japan. Unfortunately, there have been few reports [1] on this method, and a clear explanation of the mechanism for the decrease in the number of particles has not been made. In general, it is thought that the main cause of the particle generation might be the fracture of the deposit (e.g. the delamination or cracking) caused by the residual stress in the deposit. But the residual stresses, or the change of the residual stress accompanied with the substrate coating by metal spraying have not been examined sufficiently. As the first step towards clarifying these issues, a fundamental study of the residual stresses in sputtered films formed experimentally on various spray coatings was carried out.

2 EXPERIMENTAL METHOD

2.1 Specimens.

To discuss the mechanisms of particle generation, it is desirable to deal with sputtered films that have a thickness greater than a few hundred micrometers; the thickness at which particle generation begins to become remarkable. Unfortunately it required too long time to make such thick films with our sputtering equipment. Therefore, the films with a thickness of less
than 50μm, which were comparatively easy to form, were prepared. We were mainly concerned with clarifying the basic behavior of the residual stress in sputtered films on the spray coatings. TiN film, being utilized frequently in semiconductor devices, was chosen as the subject of this study. Fig.1 shows schematic illustrations of the cross-sectional structures of the specimens prepared to investigate the change of the residual stresses in the TiN films by spray coating the substrate. The components used in the vacuum chamber, as the shutter plates, the shields, and so on, are usually made of Al-alloy, so the Al-alloy plates (JIS A5052, 12 × 12 × 1 [mm²]) were used as the substrates. After being blasted by the Alumina grit, the substrates were metal sprayed with Al powder (99.7%) or Cu powder (99.99%). TiN films were sputtered on the substrate directly, and on the spray coating respectively, with the sputtering equipment (HSR-521A, Shimadzu), under the same condition for all specimens (Ar partial pressure: 2.0 × 10⁻²torr, film formation rate: 1.7μm/hour). A TiN plate was used for the target with sputtering. The boundary of spray coating and TiN film was so indistinct that it was impossible to measure the thickness of TiN film accurately. In the following, the thickness of TiN films are shown with the estimated values from the film formation times and rate; however, the thickness of TiN films sputtered on the substrates directly were confirmed to be almost equal to the estimated values by cross-sectional observation.

2.2 X-ray stress measurements.
The residual stresses in the TiN films were measured by using the X-ray stress measurement method (sin²θ method). Table 1 shows the conditions of X-ray stress measurement. Young’s modulus and Poisson’s ratio of TiN was assumed 570GPa and 0.16, respectively.

3 EXPERIMENTAL RESULT AND DISCUSSION

3.1 An example of deposit.
Prior to the experiment, the residual stress measurement and surface observation were carried out for the TiN deposit formed in an actual manufacturing process of semiconductor devices. This deposit was formed on the shutter plate made of Al-alloy, and the shutter plate was pre-coated with sprayed Cu. The area TiN deposited was slightly larger than the area Cu sprayed. In order to compare the deposit formed on the shutter plate directly and on the sprayed Cu, the sample which included both the deposits was cut from the shutter plate (Fig.2). The thickness of this deposit on the shutter plate directly was about 300μm.

Fig.3 shows a SEM photograph of the sample’s surface. The upper-half of this photograph shows the deposit formed on the sprayed Cu, and the lower-half shows the deposit formed on the shutter plate directly. In the deposit formed directly on the shutter plate, the diameter of the grains was about 100μm on average, and its dispersion was comparatively small. In contrast, in the deposit on sprayed Cu, extremely large grains which grew over 300μm were observed. It is thought that coating the substrate by metal spraying might have an effect on the grain growth of TiN.
The residual stresses in these TiN deposits were measured by X-ray stress measurement using TiN222 diffraction of Cr-Kα line. Fig. 4 shows $2\theta$-$\sin^2\psi$ diagrams for each deposit. The residual stress in the TiN deposit on the sprayed Cu and on the shutter plate directly estimated from the slope of the each diagram was -504MPa and 708MPa, respectively. It is thought that coating the substrate by metal spraying might have the effect of changing the sign of the residual stress in the TiN deposit, and the result indicated the possibility that the compressive residual stress obtained by substrate coating by metal spraying might decrease the number of particles, or delay particle generation.

As described above, it was found that metal spraying of the substrate could change the residual stress and grain growth behavior in the TiN deposit. In order to investigate the details of these changes experimentally, TiN films were formed on the various spray coatings, and the residual stresses and grain growth behaviors of these TiN films were investigated. These results are described in the following sections.

### 3.2 The changes of the residual stresses in TiN film with metal spraying to the substrate.

In order to investigate the changes of the residual stress with substrate coating by metal spraying, three types of specimens, named AP, CP, and AB, were prepared. AP and CP had a 3-layer structure of the substrate, the spray coating and the sputtered TiN, and AB had a 2-layer structure of the substrate and the sputtered TiN. In all specimens, the thicknesses of TiN films were made to be 10μm. Al powder and Cu powder were plasma-sprayed for the middle layer of specimens AP and CP, respectively. The center line average roughness (Ra in JIS) of the Al-alloy substrate was 1.1μm, and the roughness of the spray coating of AP and CP was 23.5μm and 16.8μm, respectively.

The residual stresses in the TiN films of these specimens were measured by X-ray stress measurement. Fig. 5 shows the results. In this figure, the values of the average and the standard deviation of the measurements for 12 pieces are also shown for each specimen.
The compressive residual stress was observed in each TiN film whether the substrate had been metal sprayed or not. A difference of the sign of residual stress, as described in Sect.3.1, was not observed. It was found that metal spraying could reduce the residual stress in the TiN film. Comparing with the result of AP (Al sprayed) and CP (Cu sprayed), the reduction of the residual stress in AP is larger than in CP. It is considered that the reductions of the residual stresses might depend on the kinds of sprayed materials.

3.3 The influence of the surface roughness of spray coating on the residual stress in TiN film.

A spray coating is formed by the melted metal rapidly solidifying on the substrate, so the surface of a spray coating has very complicated configuration. To specify the characteristics of the spray coating which brought such the changes of the residual stress as described Sect.3.1 and 3.2, the surface roughness was considered to be the most characteristic property of the spray coating compared to the bulk material. Consequently the influence of the surface roughness of the spray coating on the residual stress in the TiN film was investigated.

Substrates coated with sprayed Al with varying surface roughness were prepared, and TiN films were formed on each spray coating. The thickness of these TiN films was 10μm. The residual stresses in these TiN films were measured by X-ray stress measurement. Fig.6 shows the result. The error-bar shows the standard deviation of the measurements for 6 pieces of each specimen.

It was found that the residual stresses in all specimens were smaller than that of specimen AB(-796MPa as described in Fig.5). The reason may be as follows. Metal spraying the substrate increases the surface roughness of TiN film and creates many protrusions. And the constraint for the protrusion tip from the surrounding regions may decrease as the result of a lack of continuity with the surrounding regions. This may result in the decrease of the residual stress of a metal sprayed specimen compared with that of not metal sprayed specimen. Comparing only the specimens that were metal sprayed, it was also found that the residual stress might tend to increase as the surface roughness of the spray coating increases. It has been reported that the stress value evaluated by X-ray stress measurement is affected by the surface roughness of the specimen, and become smaller with increasing surface roughness [7]. But the result in Fig.6 may not correspond to this report. The reason will be discussed in Sect.3.4.
3.4 The thickness dependence of residual stress in TiN film.

For the specimens AP and AB, the thickness dependence of residual stresses in TiN films were investigated. Fig. 7 shows the results. It was observed that there was the difference in the residual stress of AP and AB as described in Sect. 3.2 at all thicknesses examined in this experiment. It was also observed that there was a similarity in the thickness dependence of the residual stresses of AP and AB; both the residual stresses decrease at the low thickness region, and then increase above 20 μm in thickness.

When the specimen AB is assumed the binding plate which consisted of two plates of TiN and Al-alloy, it is considered that the compressive thermal stress (originated from the mismatching of thermal expansion between TiN (9.5 × 10⁻⁶ 1/K) and Al-alloy (23.1 × 10⁻⁶ 1/K), and the difference between sputtering temperature and room temperature (about 100K)) decreases as the TiN thickness increases because of the increase of the cross section area which undertakes the thermal loading (as shown in Fig. 7 by the broken line). The increase of compressive residual stress observed above 20 μm in thickness in Fig. 7 could not only be explained by thermal stress. In the generation of the residual stress, factors in addition to the thermal stress must also be considered.

Note that as shown in Fig. 6 the compressive residual stress in the TiN increased with increased surface roughness of the spray coating. The reason may be as follows. The TiN thickness of the specimens used in the investigation of Sect. 3.3 was estimated to be 10 μm from the product of the film formation times and rate because of the difficulty to measure them. However, the actual thickness of the TiN might be smaller than the estimated value because of the increase of the surface area owing to the complexity of the surface configuration of the spray coating. And it might be decreasing with increasing the surface roughness of spray coating. Then, in Fig. 7, it was observed that, within 10 μm or less, the compressive residual stress was increasing with TiN thickness decreasing. These may result in the increase in the compressive residual stress as the surface roughness of the spray coating increases.

From these results, the surface roughness of spray coating is considered as one of the determinant factors of the residual stress in TiN film sputtered on spray coating.

3.5 The observations of grain growth behaviors in TiN films.

SEM photographs of the surface observed at several TiN thickness for the specimens AB and AP are shown in Fig. 8. The greater the thickness of TiN, the larger the grain size. Although the grains of the specimen AP were much larger than those of the specimen AB, the thickness at which the grains grew remarkably were almost same for both specimens about 10 μm to 30 μm. It is considered that coating substrates by metal spraying affects the grain growth rate, but do not affect so much the thickness at which grains grow remarkably.

This thickness 10 μm to 30 μm corresponds to the thickness at which the compressive residual stress changed from decrease to increase, as shown in Fig. 7. It is also considered that the grain growth might affect the residual stress of TiN film.
Fig. 8 SEM photographs of specimen's surface at each TiN thickness.

4 CONCLUSIONS

Residual stress measurement and surface observation of the TiN films sputtered on the substrates coated by metal spraying were carried out. The following results were obtained.
1) Coating the substrate with metal spraying decreased the residual stress in TiN films under 50μm thickness.
2) The residual stress in TiN film sputtered on substrate coated by metal spraying depended on the surface roughness of the spray coating, and increased with increasing surface roughness.
3) Coating the substrate by metal spraying affected the grain growth rate, but did not affect so much the thickness at which grains grew remarkably.
4) The grain growth might affect the residual stress in sputtered TiN films.
5) For the particle problem, it was insufficient only to examine the residual stresses in films with 50μm thickness or less. It is necessary to carry out the further investigation on films with a thickness of at least a few hundred micrometers.

REFERENCES