Transactions of the Materials Research Society of Japan. Vol. 20

Effects of nodules on sputtering characteristics.

K. Utsumi and A. Kondo

Tokyo Research Laboratory, TOSOH Corporation
2743-1, Hayakawa, Ayase-shi, Kanagawa-ken, Japan

Effects of nodules on sputtering characteristics were investigated for ITO target of 98% in relative density. As the target surface was covered with nodules, deposition rate decreased and discharge voltage, arcing frequency and particles increased. EPMA analysis showed that resistivity of nodule area was higher than one of normal area. This is the cause of aforesaid behavior of sputtering characteristics and particle generation. From the compositional and morphological analysis of nodules by EDS and SEM, it is indicated that nodules are formed by remainder of sputtering due to high resistivity and low sputtering yield nucleus.

1. INTRODUCTION

Thin film ITO (indium tin oxide) has been widely used as transparent conducting layers in various optoelectronic devices such as liquid crystal displays, plasma displays and solar cells. The preparation processes of ITO thin film include spray [1], chemical vapor deposition (CVD) [2], evaporation [3] and sputtering. Among these methods, the most preferred method is reactive dc magnetron sputtering using ITO target because it is advantageous in its controllability of sputtering condition and adaptability to large area sputtering [4].

In continuous sputtering of the ITO target in an atmosphere of argon and oxygen mixture gas, black nodules appear on the erosion race track of the target [5]. Because nodules are considered as a main cause of particles on substrates, demands for reducing nodules have been increased in thin film industry.

It has been reported that ultra high density targets (99% or more) and low surface roughness targets are very effective to suppress the nodule formation [6-7].

In this study, effects of nodules on sputtering characteristics such as discharge voltage, deposition rate, arcing frequency and particles stuck on the substrate are investigated to reveal the origin of particle generation. Furthermore, mechanism of nodule formation is proposed.

2.EXPERIMENTAL PROCEDURE

Continuous sputtering test was performed in a load-lock type dc magnetron sputtering system. The ITO target which contained 10 [wt.%] SnO2 was made by atmosphereic sintering. It was a 5" x 7" rectangle, and had 98% in relative density. 4" semiconductor grade Si wafers were used for substrates to measure a number of particles.

Table 1
Sputtering conditions

Sputtering method	Sputter up
Sputtering pressure	5.0 [mTorr]
DC power density	2.7 [W/cm2]
Gas flow rate	Ar:80 [SCCM] O2:1.2 [SCCM]
Target substrate distance	10 [cm]
Substrate temperature	R. T.

Sputtering conditions are shown in Table 1. Discharge voltage, deposition rate, arcing frequency and a number of particles stuck on the substrate were measured. These measurements were performed at 5 [kWh] intervals from start to 30 [kWh] in cumulative sputtering power without removal of nodules. After 30 [kWh], nodules were removed. Then, the measurements were continued.

Arcing frequency was monitored as discharge current spikes which were converted into voltage pulses by a sensing coil inductively coupled with the power cable of the sputtering source. A laser particle counter was used for the measurement of a number of particles.

Energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and electron probe micro analysis (EPMA) were used for analysis of the nodules to investigate the mechanism of particle generation and nodule formation.

3. RESULTS AND DISCUSSION

3.1 Continuous sputtering test

Volume of nodules was estimated by computer mage processing using optical photograph of target surface. The relationship between volume of nodules and cumulative sputtering power is shown in Fig.1. Volume of nodules initially increased slightly with cumulative sputtering time to 10 [kWh], and as the cumulative sputtering power increased further, volume of nodules increased rapidly. Moreove 30 [kWh], erosion race track was almost filled nodules.

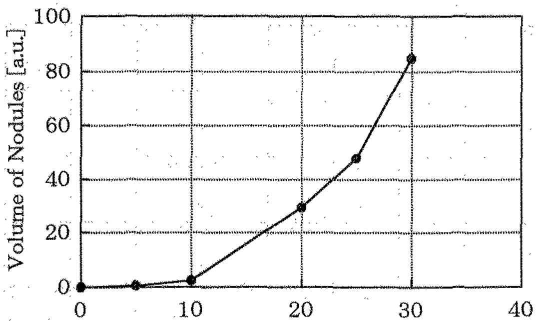


Fig.1 The Relationship between Volume of Nodules and Cumulative Sputtering Power.

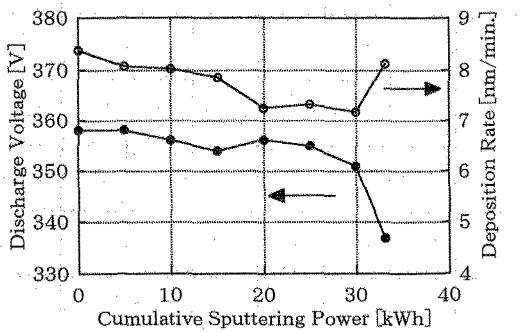


Fig.2 Dependences of Discharge Voltage and Deposition Rate on Cumulative Sputtering Power.

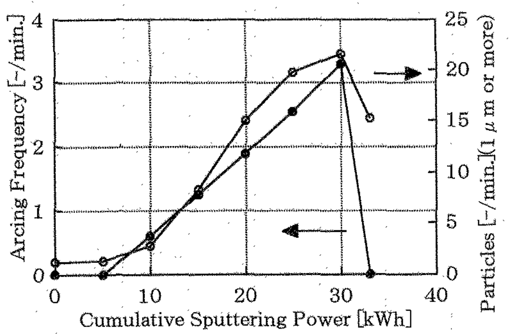


Fig.3 Dependences of Arcing Frequency and Particles on Cumulative Sputtering Power.

The dependencies of discharge volt deposition rate, arcing frequency and a numbe particles on cumulative sputtering power are sh in Fig. 2-3. Generally, discharge voltage decre with the increase of cumulative sputtering pc because substantial target thickness decreases erosion. However, from 15 [kWh] to 30 [kWh was lifted up. Furthermore, in this region, deposi rate was lowerd. These abnormal behaviors v observed during rapid increment of the volum nodules. Figure 3 indicates that arcing frequency particles increased as the target surface was cov with nodule.

Nevertheless, once nodules were removed f the target surface, aforesaid sputtering characteris were recovered rapidly to the initial state.

From these results, it was shown that a nun of particles stuck on the substrate depended arcing frequency.

3.2 Analysis of nodules

At first, composition of nodule was evalu using EDS. It was found that the nodules v composed of indium, tin and oxygen, and that it substantially ITO.

Next, morphology of nodule was studied. Fi 4 shows cross sectional SEM image of nodule was observed that the nodules had some pores in same way as normal part had pores (marked arrows). These results suggest that nodules are formed by re-deposition back to target surface by substance peeled off from sputtering chambe cluster of ITO scattered by plasma.

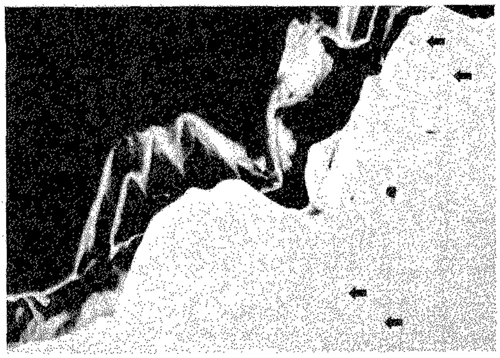


Fig.4 Cross sectional SEM image of nodules. (x750

Fig.5 Plane view SEM image of nodules. (x3000)

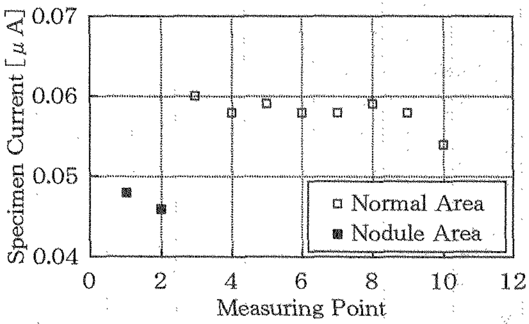


Fig.6 Specimen current at each measuring points.

Figure 5 shows plane view SEM image of the nodules in the early stage. It was observed that the nodules were formed at the edge of pores and that the nodules included white bright part (pointed No.1 and 2). Therefore, specimen current at each point marked with arrows were measured using EPMA. The results are shown in Fig.6. It was found that the specimen current at nodule area was lower than one of normal area. These results indicate that they have high resistivity and that white bright part is charged up.

It is considered that lifted up discharge voltage and lowered deposition rate described in section 3.1 are due to these high resisitivity and charged up substances, respectively.

Moreover, because nodules including high resistivity substance store electrical charge easily, arcing is generated by dielectric breakdown between high resistivity substance and electro-conductive erosion race track or hot electron introduced by concentration of electric fields. When arcing is generated, clusters of target material are splashed out and formed as particles. It is considered that these are the main cause of particle generation.

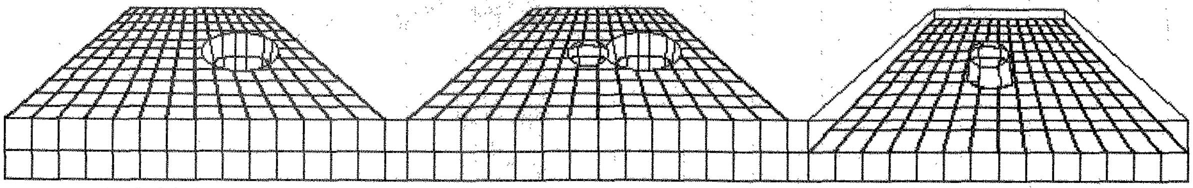
3.3 Mechanism of nodule formation

From the above mentioned analytical data, we consider the mechanism of nodule formation as follows.

Schematic illustrations of nodule formation are shown in Fig.7. Figure 7-(a) shows the initial state of the ITO target. There are some pores on the target surface.

After a few minutes sputtering, high resistivity substance, which is considered nucleus of nodule formation, is formed at the edge of pores (Fig.7-(b)). It is considered that arcing generated by concentration of electric field at the edges of pores leads nucleus formation because arcing frequency was extremely low in the case of low surface roughness target which were very effective to suppress the nodule formation. Furthermore, although the cause of high resistivity of nucleus is not proved experimentally because of difficulty of analysis of precise amount of oxygen, main cause of it is assumed to be due to the increase of scatter center by increment of oxygen vacancy led by flying out of oxygen from the target.

This nucleus was easily charged up during sputtering because of its high resistivity. Therefore, electric field is bent and the bending of electric field disturbs bombardment of Ar ion to the nucleus. On



(a) Initial state (b) Nucleus generation (c) Nodule formation

Fig.7 Schematic illustration of mechanism of nodule formation.

the other hand, erosion race track having electro-conductivity is bombarded normally. As the result, nodules are formed by remainder of sputtering (Fig.7-(c)).

Generally, ITO targets have pores not only on target surface but also inside the target. This indicates that probability of nucleus formation increases with depth of erosion.

Moreover, fresh ITO targets have many scratches on the surface by mechanical machining. These scratches are considered to lead arcing and nodule formation.

Consequently, in order to obtain particle-less ITO thin film, suppression of nodule formation is very important. Namely, the strong demands for preparation of ITO film without particle adhesion are accomplished by using ultra high density (99% or more) and low surface roughness target.

4. CONCLUSIONS

Effects of nodules on sputtering characteristics were investigated for ITO target having 98% in relative density. It is observed that as the target surface is covered with nodules, arcing and particles increase. Moreover, nodule formation leads to the decrease of deposition rate and the increase of discharge voltage. EPMA analysis shows that resistivity of nodule area is higher than one of normal area. This is the cause of increase of discharge voltage. It is also considered that because nodules easily store the electrical charge by its high resistivity, deposition rate decreases and arcing occurs which is origin of particle generation. From the compositional and morphological analysis of nodules, nodules are remainder of sputtering due to high resistivity and low sputtering yield nucleus.

ACKNOWLEDGMENTS

The authors would like to thank C. E. Wickersham, Jr. and A. Leybovich at TOSOH SMD Inc. for useful discussion of this work and suggestion of arcing measurement.

REFERENCES

1. A. K. Saxena, S. P. Singh, R. Thangaraj and O. P. Agnihotri, Thin Solid Films, 117, 95 (1984).
2. T. Maruyama and K. Fukui, Thin Solid Films, 203, 297 (1991).
3. I. Hamberg and C. G. Granqvist, J. Appl. Phys., 60, 11 (1986).
4. R. Latz, K. Michael and M. Scherer, Jpn. J. Appl. Phys., 2, 30(2A), 149 (1991).
5. T. Yokokawa, S Tanaka, K. Eshima, R. Amoh and S. Toshizawa, Shinkuu, 37, 3, 344 (1994).
6. K. Utsumi, T. Takahara, Y. Suzuki and A. Kondo, J. TOSOH Res., 38, 33, (1994).
7. K. Utsumi, Y. Suzuki, T. Takahara and A. Kondo, The 56th Autumn Meeting of JSPA, 28a-ZH-9 (1995).