P-31: Nodule Formation on Indium-Oxide Tin-Oxide Sputtering Targets

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Abstract

Nodule formation on ITO sputtering targets was investigated by stop action in-situ video observation, 3D-SIMS, and EPMA. Major cause of nodule formation is particulates from the sputtering system, less important are particulate inclusions in the target material. A nodule growth mechanism and strategies to minimize nodule formation are proposed.

1. Introduction

Transparent conductive layers for flat panel displays are deposited by partly reactive sputtering from indium-oxide tin-oxide (ITO) targets [1]. Unfortunately, black growths, or nodules, commonly form in target racetracks during ITO sputtering. As depositions proceed the increasing nodule density causes process parameters to shift and the sputtering system must be shut down to clean or replace the ITO target.

A proper understanding of nodules should suggest means of eliminating this scourge. Previous studies [2,3] do provide useful information but the problems are as yet unsolved. The experiments reported here bring a new method to the ITO nodule investigation. Stop action observation using a video camera was used to track nodules in situ as they nucleate and grow. SIMS sputtering with three-dimensional element resolution and EPMA were subsequently employed to identify possible impurities on tops of nodules and to investigate whether or not particulate inclusions in the target material might generate nodules. The results provide insight into nodule nucleation, the influence of target particulate inclusions, and the nodule growth mechanism.

2. Experimental Details

To observe the progress of nodule formation and growth a video camera with a zoom lens was aimed through a window of a Leybold Z 400 lab type sputtering system. During target operation the power was set to 80 W (2 W/cm²). Sputtering gas was the usual Ar/O₂ mixture, adjusted to obtain lowest thin film resistivity (about 180 μΩcm) for cold deposition and subsequent 200°C annealing. At intervals of 5 to 30 minutes the sputtering process was stopped and the target’s appearance recorded on videotape. Since the Z 400 sputtering system has a rotatable platform equipped with three DC magnetron cathodes there was the additional opportunity to sputter up to three targets in the row without interrupting the vacuum.

Sputtering targets were made by hot isostatic pressing partly reduced powder mixtures of 90 wt.% indium-oxide and 10 wt.% tin-oxide [4]. The metallic purity was 4N and the target density 97% TD.
3D-SIMS analyses were made with a CAMECA ims5f system using \( \text{O}^{2+} \) and \( \text{Cs}^+ \) ion beams. The achieved lateral resolution was in the range of several microns while the depth resolution is a few nanometers.

3. Results

3.1 Nodule characterization: Fig. 1 is a typical example of a nodule covered ITO target. Nodules usually are cone shaped (fig. 2, 3, 4). Occasionally, truncated cones can be observed, formed from a foreign particle or flake on the target surface which prevents the underlying ITO from being sputtered (fig. 2, 4). Figure 5 which shows the schematic cross-section through a typical ITO nodule is a composite drawing derived from numerous photomicrographs taken in this study. One can see that a nodule consists primarily of target material and is covered by a homogenous ITO overcoat, being up to several ten \( \mu \text{m} \) thick. See also figure 4. The indium/tin ratio in the overcoat (by EPMA) is close to the target’s, but there is a considerable oxygen deficit compared to the target. This is in agreement with [5].

3.2 In-situ observations: Two ITO targets of 75 mm diameter, drawn from the same production batch, were installed on the DC magnetron cathodes of the rotatable target platform. The two targets were sputtered one after the other without interrupting the vacuum. Surprisingly, the target which was sputtered at first was covered with nodules after but

Fig. 1. Picture of an eroded ITO target covered with nodules (x 0.8).

Fig. 2. SEM micrograph of cone shaped nodules. The left cone still has a particulate on its top (x 250).

Fig. 3. SEM micrograph of a truncated nodule with a large particle on top (x 2.000).
Fig. 4. SEM micrograph of a cone which lost its top. Notice the thick overcoat of redeposited ITO (x 500).

1 hour of sputtering. The identical second target remained essentially free of nodules for 4 hours. For both targets nodules grew in size and number as sputtering continued and also after 10 hours a difference in nodule density of almost two orders of magnitude was visible (fig. 6,7).

Fig. 5. Schematic cross section of a nodule on an ITO sputtering target.

In some cases the video tape revealed small white contaminant particles on the target’s surface. Some of these particles turned out to be nodule nucleation sites. Viewing individual nodules over time proved that nodules do not grow and disappear but, rather, they become larger and larger. An exception is nodules formed in the center of the racetrack. These often are sputtered away again, resulting in an almost nodule free racetrack center line (fig. 1,6).

The unexpected difference in nodule density be-
tween the first and the second target, and the video camera observations, show that the major source for nodule nucleation is dust and flaking from the sputtering machine. These particles were collected by the first target at the very beginning of the sputtering operation. The identical second target, hence, was operated under much cleaner conditions. In addition, investigations of partly eroded targets showed that the redeposited material on the target itself causes nodule formation in two ways: (1) There is a continuous transition from the central redeposit to the nodules in the racetrack. It looks as if material which was redeposited in the beginning, later on is molten during progressive sputter erosion, thus forming nodules by a kind of coagulation process. (2) SEM pictures from the central redeposit show severe flaking from film disintegration (fig. 8). A further source for particulates are joins between tiles in segmented target constructions. In these gaps dust may collect and excessive formation of redeposits takes place. This explains the general observation that nodule density is higher in the vicinity of joins between target tiles. See fig. 1.

SEM micrograph of the ITO target’s central redeposit (x 200).

3.3 SIMS and EPMA analyses: In several cases it was possible to identify SiO$_2$ and Al$_2$O$_3$ particles at the nodule’s peak. These were clearly traced to sputtering machine contamination. Purposely salting ITO targets with ceramic particles (SiO$_2$, Al$_2$O$_3$, TiO$_2$, C) during the manufacturing process resulted in the expected nodule formation under these inclusions since they show a lower sputter yield than ITO. In another test, SIMS sputtering through a 50$\mu$m large C particle, incorporated in the target material, created a distinct ITO nodule.

4. Discussion

4.1 Nodule growth mechanism: This study shows that particulates nucleate cone shaped nodules by shielding the target material underneath from being eroded. The particulates may originate in the sputtering system or process (principal cause) or from inclusions in the target material (secondary cause).

Immediately after nucleation by a particulate the nodule starts to be coated with an ITO film which comes from sputtering of the surrounding target material. This mechanism is sketched schematically in figure 5 in analogy to [6,7]. Because of oxygen starvation near the target surface the nodule overcoat is oxygen deficient and of low electrical conductivity [5]. The sputtering yield is thus lowered, so that nodules tend not to erode away. On the contrary, the overcoat appears to grow considerably until it cracks under thermal stress or is destroyed by a micro arc. Nodule breakups (fig. 2, 4) plausibly generate particle showers which may nucleate a new generation of nodules. This would explain the observation that, once started, nodule growth advances rapidly. In the racetrack centerline conditions are somewhat different than elsewhere. The ion bombardment and surface temperature are high enough to destabilize the nodule overcoat. Here contaminant particles usually etch away cleanly after a certain time without forming black growths.

4.2 Suggestions for minimizing ITO nodules: The system, cathode, and process designs must be op-
timized to control particulate target contamination. Specifically, (1) sputtering machines should be designed and maintained using the best particle control strategies, (2) cathodes should be engineered to minimize redeposition on the target, and, (3) target thermal cycling should be minimized to reduced flaking of back sputtered material.

Target manufacturing should be controlled to minimize particulate inclusions, and a sound microstructure provided to minimize ITO spalling from the target. Implementing these precautions can produce essentially nodule free ITO sputtering.

5. Conclusion

Using stop action in-situ video observation during target erosion together with 3D-SIMS and EPMA analyses, the mechanism for nodule growth on ITO targets could be unraveled. ITO nodules are nucleated predominantly by particulates generated in the sputtering system or process. Ceramic particulate inclusions in the target material show a similar effect but are of minor importance. In the early stage nodules are cone shaped with the particulate on the tops. Once generated, nodules are stabilized by a redeposited ITO overcoat with strong oxygen deficit, having a lower sputtering rate than the surrounding target material.

As a consequence, sputtering machines, cathodes, and target materials should be designed to minimize all possible sources which may generate particulates. The focus should be on system cleanliness and redeposition free target erosion.

Acknowledgement

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References:

[4] US patent 5,480,652 and German patent 41 24 471