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ADVANCED TRANSPARENT CONDUCTIVE OXIDE ELECTRODE FOR OPTOELECTRONIC THIN-FILM DEVICES

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Electrodes for optoelectronic thin-film devices must be conductive, optically transparent, and structurable by etching. The indium-tin-oxide (ITO) currently used fails to meet all these requirements. A new deposition sequence for ITO is therefore proposed. ITO films are grown reactively by magnetron sputtering from an indium/tin target. During the process, the oxygen partial pressure is varied periodically. We investigated the microstructure of these films by cross-sectional transmission electron microscopy (TEM) and show results of conductivity, optical absorption and etching behavior.

1 INTRODUCTION

Transparent electrodes are required for many kinds of optoelectronic thin-film devices[1], e.g. image sensors based on amorphous silicon[2,3], liquid-crystal displays[4] or solar cells[5]. The electrode material must therefore meet the following requirements simultaneously:

- optical transparency (normally in the visible spectral region)
- electrical conductivity (value depending on the specific application)
- structurability by photolithography and etching

As the transparent electrode is often placed on top of the semiconductor, the maximum temperature for its production is limited. Thus indium-tin-oxide (ITO) is commonly used, since it can be deposited at room temperature by evaporation[6] or sputtering[7] and must be annealed only at moderate temperature (≈200°C). These films exhibit a transparency > 80 % and a conductivity > 100 S/cm. Due to their microstructure, the films can hardly be etched by HCl or by H_2SO_4. More agressive acids, however, cannot be used, as they might destroy previous layers of the device (e.g. a metallic bottom electrode).

2 EXPERIMENTAL DETAILS AND RESULTS

ITO films were deposited on glass substrates by reactive magnetron sputtering of a metallic target, composed of 90 % indium and 10 % tin. The gas used for sputtering was a mixture of 3×10^{-3} mbar Ar with up to 2.6×10^{-3} mbar O_2 added. The film thickness amounted to about 100 nm. After producing a resist mask and wet etching in 5 % HCl in H_2O, the patterned films were annealed for 1 h at 200°C in an O_2 ambient. Details will be published elsewhere.

As shown in Fig.1, the transmission and sheet resistance depend critically on the O_2 partial pressure. At 1.6×10^{-3} mbar of O_2, ITO films with > 70 % transparency and < 1600 Ω sheet resistance are produced which can be etched with diluted HCl at a rate of about 1 nm/s. Unfortunately, this reactive sputtering process is rather irreproducible. For stable production, the condition of the target surface is of crucial importance. During the sputtering process, the target becomes oxidized. This alters the deposition rate[8] and thus the microstructure of the growing film. Although the oxide contamination of the target was removed prior to each run by presputtering in pure argon for several minutes, it was not possible to establish a reliable process.

To clarify the instability of the sputtering process, we investigated the microstructure of the ITO films by cross-sectional transmission electron microscopy (TEM)[9]. Different types of ITO films were found. Films sputtered with a low O_2 partial pressure (< 10^{-3} mbar) at a high deposition rate (> 0.4 nm/s) exhibit rather rough surfaces. They are mostly amorphous (Fig.2) with only few crystallites embedded. The grains of all observed samples consist of Sn-doped In_2O_3 as found by electron diffraction and energy dispersive X-ray spectroscopy in a TEM[10]. Oxygen-deficient films are highly conductive but of minor transparency. They can be etched very fast due to their amorphous matrix.

ITO films sputtered with higher O_2 pressure (> 2×10^{-3} mbar) at a lower deposition rate are crystalline (Fig.3) with a compact, about 20 nm thick bottom layer followed by columnar grain growth. These grains reach

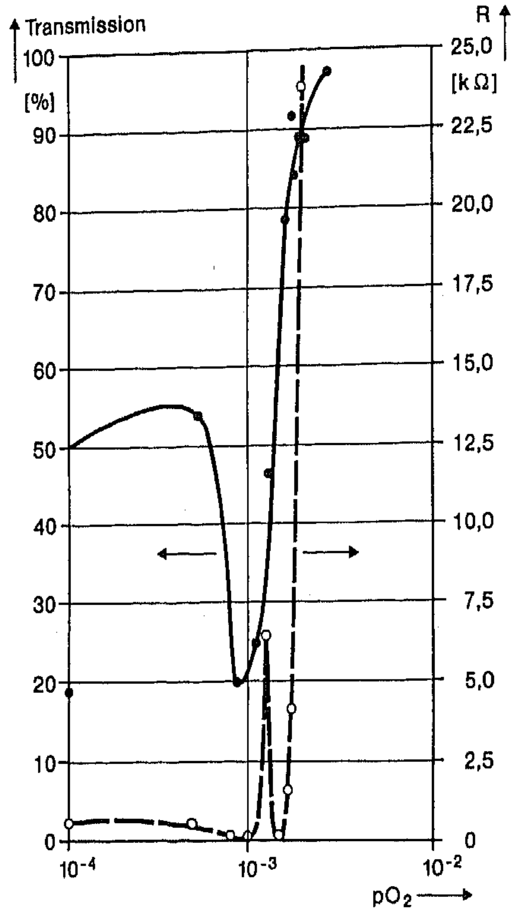

Fig.1: Dependence of the optical transmission (left scale) and the sheet resistance R (right scale) of about 100 nm thick ITO films on the O_2 partial pressure during the sputtering process. ITO with good properties can only be produced at a narrow partial pressure range of O_2 around 1.6×10^{-3} mbar.

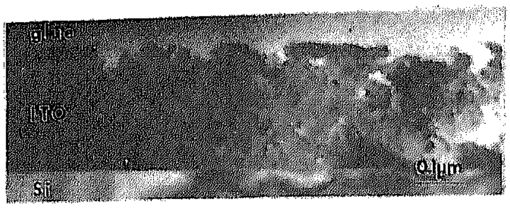

Fig.2: TEM cross-section of an ITO film sputtered with a low oxygen pressure. The film is mostly amorphous with a few crystallites enclosed.

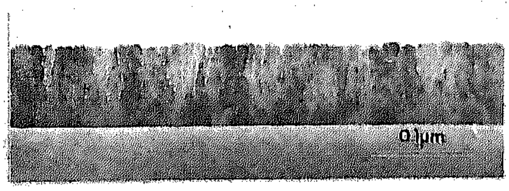

Fig.3: TEM cross-section of an ITO film sputtered with a high oxygen pressure. The film is crystalline.

Fig.4: TEM cross-section of an ITO film sputtered with 1.6×10^{-3} mbar oxygen pressure. The film starts growing in an amorphous pattern. After 50 nm it changes partially to a crystalline microstructure with numerous vertical pores separating different grains.

Fig.5: TEM cross-section of an ITO film deposited with periodically varied oxygen content. The film consists of many grains with small amounts of amorphous material in-between. The layered deposition sequence is not visible.

mostly throughout the whole ITO layer with a lateral size of approximately 20 nm and are seperated by vertical pores forming something like a honeycomb structure. These films are highly transparent but of low conductivity (due to the pores). They can hardly be etched even after several hours of etchant exposure due to the compact bottom layer.

It is known from our investigations[10] that crystalline layers penetrated by vertical pores like the upper part of the ITO film shown in Fig.3, and layers with amorphous microstructure exhibit a high etching rate. A film consisting of both amorphous material and a porous region with crystallites is shown in Fig.4.

However, ITO films with a porous microstructure may be penetrated for example by water vapour. This can influence the interface between ITO and amorphous silicon which gives degradation risks for the performance of according devices, e.g. image sensors[11,12].

To overcome all these difficulties, we propose a new deposition method. We produce an ITO "multilayer" with varying oxygen content by altering the O_2 partial pressure in the sputtering gas periodically between a high and a low level during deposition. The high O_2 pressure was 1.6×10^{-3} mbar, the lower one was kept at different values below 2×10^{-4} mbar. The whole film is formed by up to 40 "layers", the oxygen-poor and the oxygen-rich "layers" being sputtered for 5 - 30 s and 10 – 60 s, respectively.

Fig.5 shows a film consisting of 16 "layers" with a total thickness of 100 nm. The deposition started with an oxygen-poor "layer", sputtered for 5 s, followed by an oxygen-rich "layer", sputtered for 40 s. This sequence was repeated 8 times. In the TEM image, however, no distinct layered structure can be seen. The microstructure exhibits grains with thin regions of amorphous material in-between.

The electrical, optical and etching properties of these ITO "multilayers" are markedly better than those of the single layers described above. They are as follows:

- sheet resistance < 600 Ω
- optical transmission > 85 %
- etching rate in HCl > 3 nm/s

3 DISCUSSION

Photolithographical patterning of ITO films by wet chemical etching has hitherto been a serious problem in using ITO as a transparent electrode in thin-film devices. The cross-sectional TEM investigations demonstrate that an ITO film has to be either amorphous or must have many vertical pores in its crystalline part if it is to be etchable. The ITO "multilayers" exhibit a high etching rate, since such films consist of very small crystallites imbedded in an amorphous matrix. The etching agent can dissolve the amorphous part of the film, thus lifting off the grains.

To explain the generation of such a finely grained material, we suggest the following model. Sputtering an oxygen-poor "layer" leads to an almost metallic amorphous phase on the substrate. As we discovered during other experiments, a sputtered metallic indium-tin alloy tends to coalesce to small amorphous islands. As shown above, oxygen-rich ITO forms a single coherent crystalline layer. The oxygen-poor islands inhibit the growth of a continuous crystalline film. Therefore, many grains several nm in size are growing which are seperated by amorphous material and numerous pores.

As the metal-rich islands form only a small fraction of the film, they do not influence its transparency. On the other hand, these islands are etched very fast, as described above. The sheet resistance of the "multilayer" films (600 Ω) is too high for solar cell applications. This is due to the low annealing temperature of only 200° - 250°C which should not exceed the deposition temperature of the underlaying amorphous silicon. Since in image sensor applications the signal currents (≈1 nA) are much lower than the output current of solar cells (≈10 mA) they are not affected by sheet resistances of the ITO electrodes up to 1 kΩ. However, the "multilayer" deposition could probably be optimized in order to meet also this requirement.

When using ITO films in thin-film devices, the patterning capability is of utmost importance. In large-area applications (25 cm in size or more) involving image sensors or liquid crystal displays, the transparent conductive layers must be structured by wet chemical etching, since it is difficult to carry out a photolithographical lift-off process homogeneously on such a large area. The required pattern resolution is in the order of 2 - 5 μm, i.e. only small underetching of the resist mask is tolerable. Single layers of ITO show rather strong underetching which may exceed several μm. This makes it impossible to produce fine structures photolithographically. The "multilayers" allow very well- defined structures to be etched, where lateral underetching can be kept below 200 nm.

"Multilayer" ITO leads to transparent conductive electrodes which can be etched at a high rate with very small underetching. Such ITO films can be produced by simply modulating the oxygen partial pressure during sputtering. The properties of the ITO films produced in this way are much more reproducible than those of conventional single layer films.

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