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Fabrication of ZnO based transparent conducting oxides by sputtering combined with solid phase crystallization : a way to meet the future demand for transparent electrodes

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Photovoltaic (PV) market is now expanding at unprecedented pace as we strive to climate change impacts. However, the most widely used transparent electrode in PV devices, In2O3:Sn (ITO), has a key drawback that it contains rare metal and is not sufficient to meet the future demands. ZnO based transparent conducting oxides (TCOs) thus have regained a huge interest as the alternatives because of the wide band gap, the high doping efficiencies, and most of all, the material abundance. The resistivity of the films fabricated by conventional sputtering, however, is not low enough due to the poor crystal quality, still limiting the replacement of ITO electrodes. Here we report a new fabrication method that enables us to make ZnO TCOs with low resistivity comparable to that of ITO, where a seed layer is firstly fabricated via solid phase crystallization (SPC), and ZnO:Al electrode is then deposited on it [1,2]. SPC has been known to be a powerful method to achieve high crystal quality because crystal growth proceeds under thermal equilibrium conditions. Though this method was hardly applicable to ZnO due to the difficulty in forming the amorphous (a-) phase, we have realized it by sputter deposition of a-ZnON film, which itself is fabricable only under non-equilibrium condition, followed by annealing to desorb nitrogen and to promote crystallization under a thermal equilibrium condition.

We prepared 10-nm-thick seed layers on quartz glass substrates by sputtering deposition of ZnON in Ar/N_2 at room temperature, followed by air annealing at 300–600°C. Then 30-nm-thick ZnO:Al films were deposited by sputtering on the seed layers in Ar at 200°C.

We have succeeded in fabrication of a-ZnON films and thus in fabrication of ZnO films via solid phase crystallization. Extended x-ray absorption fine structure (XAFS) measurements revealed that the SPC brings about more ordered atomic arrangements in the grain interiors, causing the drastic improvement in the crystal quality. We also found that using such films as seed layers brought about improvement in electrical properties of ZnO:Al films. The resistivity of 30-nm-thick ZnO:Al films on the seed layers is low of 8×10^{-4} Ω·cm, 40% lower than that of conventional ZnO:Al films. Here the seed layers were fabricated via 600°C annealing of fully-amorphous ZnON films.

Next, aiming to further reduce the resistivity of ZnO:Al films and to lower the SPC temperature, we synthesize seed layers prepared via SPC of not fully amorphous but fractionally crystallized (fc-) ZnON films, where the degree of crystallization is controlled by controlling the geometric relationship between the sputtering targets and the substrates. Since the crystal nucleation finishes during deposition and atoms do not have to overcome a higher energy barrier to nucleate during SPC, the new seed layers are expected to bring about lower SPC temperature as well as to enable us to control the nucleation and the subsequent crystal growth independently.

The resistivity of ZnO:Al films on the seed layers fabricated via 300°C anneal of fc-ZnON films is surprisingly low of 3.2×10^{-4} Ω·cm,. This value is four times lower than that of conventional one fabricated without seed layers and still 2.5 times lower than that of above mentioned one using SPC seed layers fabricated via 600°C anneal of a-ZnON. Atomic force microscopy measurements revealed that the seed layers grown from fc-ZnON have more uniform grain size distribution than that grown from a-ZnON have, considered to be due to the shorter period of nucleation occurring, that is, the nucleation might occur only during the film deposition as we expected. In fact, we observed that the activation energy of crystal growth during SPC of fc-ZnON is low of 0.22 eV, about one half of that of a-ZnON, indicating that no nucleation occurred, and crystals just grew originating from nuclei embedded in the fc-ZnON during SPC. The resultant seed layers grown from fc-ZnON films, therefore, possess smoother surfaces and higher crystal quality despite the low anneal temperature, and these are the reasons why 30-nm-thick ZnO:Al films with surprisingly low resistivity has been realized by using the new seed layers.

We believe our findings offer a new pathway to meet huge TCO demands in the coming decades.

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