Effect of Electron Beam Annealing Duration on the Optical-Electrical Properties of ZnO Thin Films

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Zinc oxide (ZnO) is one of the most promising transparent conductive oxides due to its relatively low cost, nontoxicity, high chemical and thermal stability. ZnO is a native n-type semiconductor with a direct wide band gap of 3.36 eV[1], which determines it is conductive and transparent in visible range. Generally pure ZnO presents high-impedance state. The conductivity can be improved by increasing oxygen vacancy or doping with IIIA (B, Al, Ga, In), IIIB (Sc, Y, La), IVA (Ti, Zr, Hf) and IVB (Si, Ge, Sn) elements and non-metal anions, such as Cl and F[2]. EB annealing in vacuum with high energy density and cooling rapidity is a promising method to prepare ZnO with high optical-electrical performances. Vacuum annealing atmosphere can help to increase the concentration of oxygen vacancies and cooling in vacuum rapidly can prevent the diffusion of oxygen back into the ZnO film[3-5], which hence can improve the optical-electrical properties of ZnO film.

Here we mainly study the effect of EB annealing duration especially ultrashort time on the optical-electrical properties of pure ZnO thin films. Pure ZnO precursor films prepared by sol-gel spin coating method were directly annealed by EB for different time from 20 s to 480 s. X-rays diffraction patterns showed (002) preferential growth in all ZnO films. SEM and AFM studies revealed that the average grain size ranged from 10 nm to 65 nm with the increase of annealing duration and the surface RMS roughness of the films was less than 3 nm. From optical transmittance spectra, the absorption edge of the films was determined to be at ~380 nm with > 85% transmittance in visible region.

The results showed that the crystallization of ZnO film was enhanced and grains turned larger with expanding annealing duration. The film annealed for 480 s presented the highest transmittance close to 94% due to less scattering of photons. It's exciting to find that the ZnO film annealed for just 120 s exhibited resistivity value of 2×10^{-2} Ωcm and carrier concentration as high as 5.5×10^{19} cm^{-3}, which showed a huge advantage of EB annealing in the preparation of ZnO transparent conducting thin films.

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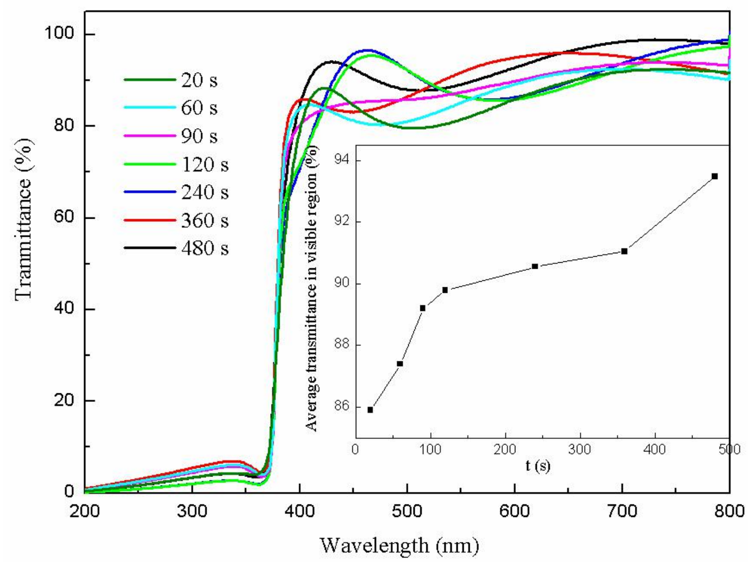

Fig. 1: The transmittance of ZnO films in UV-visible band with different annealing time: When the annealing duration was less than 120 s, the film crystallized better and the grain size was larger with expanding annealing duration. The number of grain boundary reduced, so did grain boundary scattering of photons and hence the transmittance increased rapidly. When annealing duration was in the range from 120 s to 360 s, the larger hole size and surface roughness increased scattering of photons, so the transmittance increased slowly. The ZnO film annealed for 480 s presented the highest transmittance close to 94% due to its large grain and relative small holes.

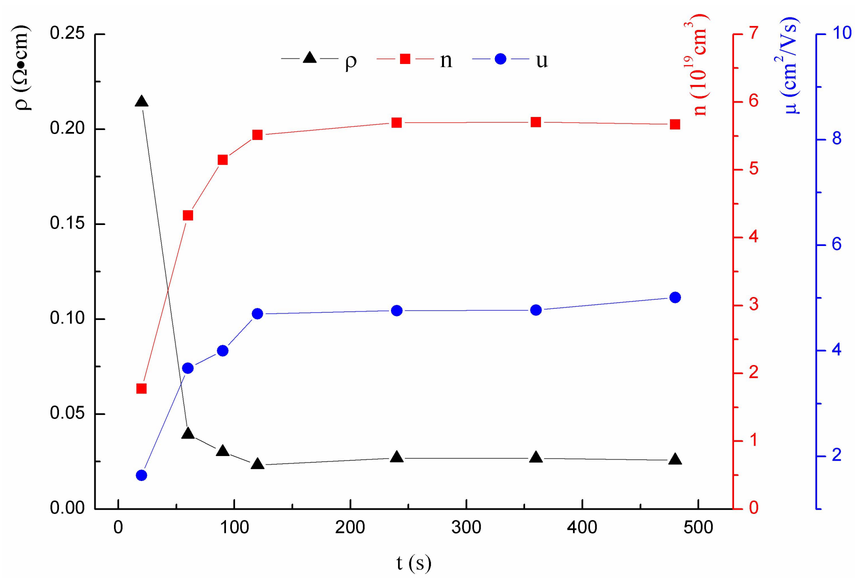

Fig. 2: The change curves of resistivity (ρ), carrier concentration (n) and Hall mobility (μ) of ZnO films with annealing duration: When annealing duration was less than 120 s, poor crystallization and small grains increased grain boundary scattering. When annealing duration was more than 120 s, the increase in impurity scattering like holes and decrease in grain boundary scattering almost balanced. So the mobility increased firstly and kept at a high value later.