

Adsorption and Desorption of Oxygen on the Surface of Polycrystalline ZnO Films Deposited by r.f. Sputtering*

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Abstract Hexagonal ZnO films with the preferred growth orientation of *c* axis parallel to the substrate have been deposited by r.f. sputtering. An electrical field induced oxygen adsorption was observed on these films. Oxygen adsorption produced by illumination of a UV light or/and reaction with Ar plasma increased the conductivity of the films by 6-7 orders of magnitude and an accumulation layer displayed on the surface of the films.

Keywords: ZnO, Adsorption, Desorption, Photodesorption, Photoresponse

ZnO films have been investigated extensively because of their wide application. An important property of this material is its strong oxygen adsorption which can be verified by various desorption (such as photodesorption). Photoresponse study is a common method to investigate this phenomenon. Many studies have been performed on the mechanism of photoresponse of the crystal, pressed powder and sintered ZnO^[1-5]. It is found that an adsorbed oxygen atom (or molecules) can capture an electron from the conduction band and makes the surface negatively charged. A depletion layer is produced beneath the surface, which will pronounced decrease the surface conductivity of the samples. When an UV light is presented, photogenerated holes will be driven by the electric field in depletion layer moving forward to the surface and neutralize adsorbed oxygen. This process is so called photodesorption and it makes surface conductivity increase significantly. When the UV light is turned off, adsorption of oxygen occurs and it will reduce the conductivity again. Another method reported for producing oxygen desorption is exposure of the ZnO to thermalized He⁺ ions, produced in an electrical discharge through helium gas at atmospheric pressure^[6].

Here we are reporting some results of oxygen adsorption and desorption occurring on the surface of polycrystalline ZnO films deposited by r.f. sputtering. Oxygen desorption produced by the reaction with Ar plasma is first reported.

1 Experimental

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The preparation of the ZnO films and their photoresponse measurements have been reported previously^[7]. The sample conductance in inert gas plasma was measured in the sputtering system. A Penthervac GPT-450 Vacuum Gauge which includes a thermistor section and a Type GPH-001 Penning Gauge was used to measure the pressure of the system. As Ar⁺ source, the Penning Gauge could introduce a visible, small-area, low-power discharge, approximately 20cm from the sample, and the resulting plasma depended on the pressure of the inert gas leaked into the system. The discharge was observed only at Ar pressure between 1.57 and 4.0 Pa. At 2.0 Pa, the film conductance reached its maximum.

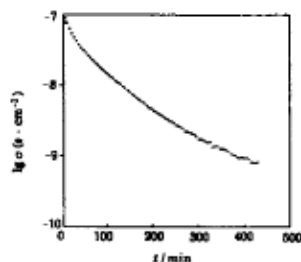


Fig.1 Variation of the conductivity vs time for a ZnO film when an electric field was first applied to an as-made sample mounted

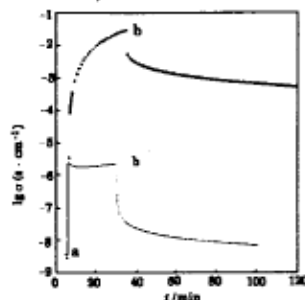


Fig.2 Vacuum photoresponses of a sample vs. time
At a, the UV light is on, at b, the UV light is off.

2 Results and discussion

The ZnO film with 500 nm thick have a average transmission exceeding 90% in the wavelength range of the visible spectrum. All samples which exhibited a large oxygen desorption had crystallites with mixed orientation having the (100) and (110) peaks dominant in the X-ray diffraction spectra.

2.1 Field induced adsorption of oxygen

Samples stored in air with an electric field first applied always show a steady decrease in the conductivity over time. This is a very slow process and takes a few hundred minutes to reach equilibrium. In this process the conductivity of the films decreases by one half to two orders of magnitude. Figure 1 illustrates this for one sample mounted in air. This may be attributed to the chemisorption of oxygen from the air and the electric field assists the adsorption and subsequent chemisorption process. Tansley *et al.*^[8] observed field-induced deionization when an electrical field was first applied to a ZnO film deposited by sputtering and it made the conductivities increase to two to five times the initial value within 15–20 min.

2.2 Photodesorption on the surface

The photoresponse of a typical new sample is shown in figure 2 as solid line. Both the rise and decay are relatively fast. However, after these samples have been exposed to air for several months the photoresponse becomes larger and the rise and decay times become much slower. The changed photoresponse is illustrated in figure 2 in circles. The

magnitude of the response is as high as 7 orders. As mentioned above, this photoresponse does not originate from true photoconductance which should produce a very fast photoresponse but comes from photodesorption of adsorbed oxygen when UV light is on and readsorption of oxygen when UV light is off.

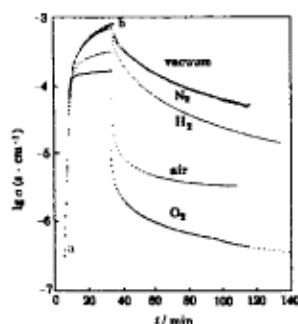


Fig.3 Photoresponse of a ZnO sample when it was mounted in vacuum and different ambient gases

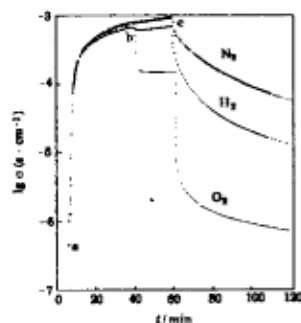


Fig.4 The effects of ambient gases on the Photoresponse for the same sample as shown in figure 3

Photoresponse change with time for ZnO films has not been reported. It can be attributed to the structural relaxation on the surface of the investigated films. ZnO has a tendency to lose its oxygen and become non-stoichiometric^[3]. After a long time some oxygen near the surface of the films is lost. The oxygen vacancies left near the surface act as donors and create a high conductance layer—accumulation layer. This effect further stimulates oxygen to be adsorbed on the surface and subsequently becomes chemisorbed by capturing one of the free electrons from the accumulation layer. The presence of the accumulation layer on ZnO surface has been reported by some authors^[4-6]. When illuminated with UV light, photodesorption takes place and the freed electrons return to the accumulation layer allowing the neutralized oxygen to desorb from the surface. The resulting changes in the surface conductance leads to large changes in the sample conductance for a high resistance sample. For the newly made sample, the accumulation layer do not form completely, hence, the photoresponse is much smaller and faster.

The characteristics of the photoresponse of the ZnO films strongly depend on the ambient gases around the sample. We have reported the dependence of the photoresponse of ZnO films, obtained by annealing samples prepared by Ion Beam Assisted Reactive Deposition, on different ambient gases (O_2 , N_2 , H_2) at one atmospheric pressure^[9,10]. The similar results were observed for sputtered ZnO films. Figure 3 shows the photoresponse of one sputtered ZnO sample in either a vacuum or in different gaseous environments (all at one atmosphere). At a, the sample was irradiated with the UV light. At b, the UV light was turned off and from b on, the decay process occurs. Figure 4 further represents the influences of the ambient gases O_2 , N_2 and H_2 on the photoresponses of the ZnO film. The film was initially illuminated in a vacuum, (a to b), then different gases (at a atmospheric pressure) were introduced into the chamber while the sample was still illuminated. At c, the UV light was turned off and the decay process occurred in the different ambient

gases indicated. These experiments further prove that oxygen desorption and readsorption control the photoresponses of ZnO films.

2.3 Oxygen desorption by reaction with Ar plasma

Oxygen desorption of ZnO films can be observed when the films are mounted in an inert gas plasma. He and Ne plasmas produced only weak reaction with adsorbed oxygen increasing the conductance by 2 or 3 orders of magnitude. Ar and Kr plasmas produced very strong response to film conductivity and increased the sample conductance by 5 or 6 orders of magnitude. The increased conductance partly produced by the Ar plasma which can conduct electrical current directly. But the conductance of Ar plasma was two orders of magnitude smaller than that produced by oxygen desorption of the ZnO sample.

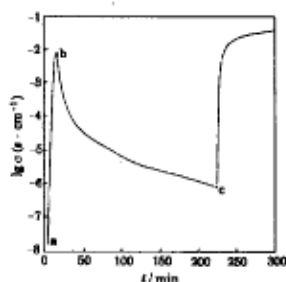


Fig.5 The time dependence of conductivities for a ZnO film

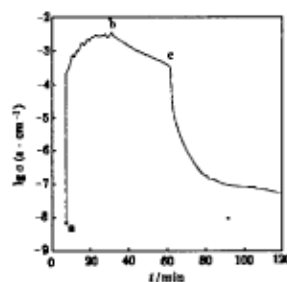


Fig.6 Conductivities of a ZnO film vs. time

As mentioned above, a chemisorbed layer of an active species (probably oxygen) depletes the surface layer converting the sample to a high resistance film. Any mechanism that can remove this chemisorbed layer can convert this high resistance film to a lower resistance sample. When the ZnO sample with its negatively charged surface, is exposed to Ar^+ ions, the chemisorbed species can be neutralized. With the loss of the adsorbed layer, the accumulation layer returns. For these samples, the availability of the Ar^+ ions controls the conductivity.

The accumulation layer formed in this way is similar to that created by the photodesorption. Figure 5 shows both the effect of photodesorption and an Ar plasma on the average conductivity of a ZnO film. Initially, the sample mounted in a vacuum chamber ($1.3 \times 10^{-3} \text{ Pa}$) was irradiated for 10 minutes with the UV light (from a to b), then allowed to relax in the dark (from b to c). During the period from b to c, it is assumed that chemisorbed oxygen returns, but the process is slowed by the partial vacuum. At c. pure Ar was introduced at a pressure of 2 Pa and the conductivity rapidly increased by ~ 3 orders of magnitude, then increased further to saturation. This rapidly increased conductance is mainly due to conductance of Ar plasma and the further increased conductance comes from the accumulation layer on the surface of ZnO films. The difference between photodesorption and ion desorption is that for the former process, photogenerated holes from the ZnO neutralized the chemisorbed oxygen releasing it from the surface, i.e. electrons are transferred from the surface to the bulk. For the latter process, Ar^+ is attracted to the negatively charged surface and captures the trapped electrons, neutralizing both the

Ar⁺ and the O⁻. The continuing presence of a source of Ar⁺ ions maintains an oxygen-free ZnO surface.

The oxygen desorption by reaction with Ar plasma is confirmed by the results shown in figure 6. An oxidized sample was mounted in the vacuum chamber. At point a, Ar is admitted to the chamber at a pressure of 2 Pa, At point b, the Ar source is turned off and the pressure in the chamber decreased rapidly to 1.3×10^{-3} Pa. At c, oxygen was introduced at a pressure of 2 Pa. This result is the similar as that mentioned above following photodesorption and the subsequent chemisorption of oxygen on the same material.

3 Conclusion

Strong oxygen adsorption and desorption were observed on the surface of polycrystalline ZnO films with mixed growth orientation of *c* axis parallel to the substrate deposited by r.f. sputtering. An electrical field induced oxygen adsorption was measured for these films. Newly-made ZnO films have relatively weak photodesorption. However, after the samples are exposed to air for a long time, photodesorption became very strong due to structural change. The surface effects of the ZnO films can be verified by observing ambient environment dependence of photoresponse and conductance in Ar plasma. Ar⁺ ions can react with negative oxygen chemisorbed on the surface, makes the adsorbed oxygen desorbed and an accumulation layer returned, consequently makes conductivity increase.

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射频溅射制备的多晶 ZnO 膜表面氧的吸附和脱附

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摘要 多晶的六角密排的 *c* 轴平行于衬底的 ZnO 膜已用射频溅射的方法制备出来. 一电场感应的氧吸附在这些膜上被观察到. 由紫外光照射或与 Ar 离子反应所产生的氧的脱附可使膜的电导率增加 6-7 个数量级, 并且一个积累层在膜的表面显现出来.

关键词: ZnO, 吸附, 脱附, 光脱附, 光响应