

# Investigation on ultraviolet photoconductivity in p-type ZnO thin films

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## Abstract

The authors report on comparative study on ultraviolet (UV) photoconductivity of p-type ZnO:N films and n-type ZnO epilayer. As compared with the ZnO epilayer, the ZnO:N films show much higher photoconductivity but with faster decay. Surface adsorption of C and O, as identified by X-ray photoelectron spectroscopy, is believed to be a major contribution to the UV photoconductivity. The surface adsorption and photodesorption process, combined with a competition between holes and electrons, in p-type ZnO:N, is proposed tentatively, providing qualitative agreement with the observed behaviors.

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## 1. Introduction

The need for blue and ultraviolet (UV) solid-state emitters and detectors has propelled the investigation on several wide-bandgap semiconductor materials in recent years. ZnO is considered to be a promising candidate principally because of its large exciton binding energy of 60 meV and the availability of large-area single crystal [1,2]. Nominally undoped ZnO typically exhibits n-type conductivity, which has been ascribed to various mechanisms including interstitial hydrogen and native defects [3–5]. The realization of p-type material, however, has long proven difficult due to its asymmetric doping limitations [6]. Fortunately, by virtue of the considerable worldwide efforts, various elements have been used as the p-type dopants for ZnO, such as N [7–9], Li [10,11], P [12,13] and As [14]. Especially, encouraging results have been recently demonstrated on ZnO homojunction light-emitting diodes [12,15–18]. Despite of these breakthrough, the reproducibility, as well as stability, of p-type material remains to be solved before further development of high-efficiency homojunction devices [19]. Clafin et al. claimed that UV illumination will significantly influence the conductivity of p-type ZnO [20]. Besides, the

reports on UV photoconductivity of p-type ZnO are currently very limited. In these regards, the origin of UV photoconductivity in p-type ZnO films is discussed in this Letter, in an attempt to address the reproducibility and stability surrounding this material.

## 2. Experiments

N-doped, p-type ZnO thin films were grown on a plane (11 $\bar{2}$ 0) sapphire substrates by a plasma-assisted metalorganic chemical vapour deposition (MOCVD) method. NO plasma, generated by a radio-frequency plasma source, was employed as both the oxygen source and the N-doping source. The growth temperature was 400 °C. Detailed growth procedures were published elsewhere [9]. Comparatively, nominally undoped n-type ZnO epilayer was grown using normal N<sub>2</sub>O as the oxygen source. The UV photoconductivity was investigated by using a 254-nm light as the illumination source. Hall-effect measurements were carried out in the van der Pauw configuration (BIO-RAD HL5500PC) at room temperature. The surface morphologies of ZnO:N films and ZnO epilayer were characterized by field-emission scanning electron microscopy (FE-SEM FEI Sirion 200 FEG). The surface adsorption was analyzed by X-ray photoelectron spectroscopy (XPS Thermo ESCA-LAB 250, Al K $\alpha$  radiation source  $h\nu = 1486.6$  eV).

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### 3. Results and discussion

Fig. 1 compares the UV photoconductivity of ZnO epilayer and p-type ZnO:N films with different thicknesses. If  $I_0$  and  $I_{\text{peak}}$  represent the original current and peak current after UV illumination, respectively, the ratio of  $I_{\text{peak}}/I_0$  for the ZnO epilayer (1.12) is significantly smaller than that of the 400-nm ZnO:N film (11.3). The ratio further increases to 16.2 for the 200-nm ZnO:N film. Also, after the UV light is cut off, the current of ZnO:N undergoes a much faster decay in comparison with ZnO epilayer. Note that the visible light exposure causes little variation of the conductivity in the present case.

In addition to the UV photoconductivity, the conduction type of ZnO:N should be concerned considering that a persistent n-type photoconductivity in p-type ZnO has been reported [20]. Fig. 2 summarizes the statistical results of Hall-effect measurements on the ZnO:N before and after UV illumination. Before illumination, the ZnO:N films show definitive p-type signals, with the hole concentrations centralized around mid- $10^{17}$ – $10^{18}$   $\text{cm}^{-3}$ . The hole concentrations, however, increase (up to  $10^{19}$   $\text{cm}^{-3}$ ) and become scattered after UV illumination. Also, Hall-effect measurements occasionally give n-type conductivity for the ZnO:N. Nevertheless, the ZnO:N films basically keep p-type con-

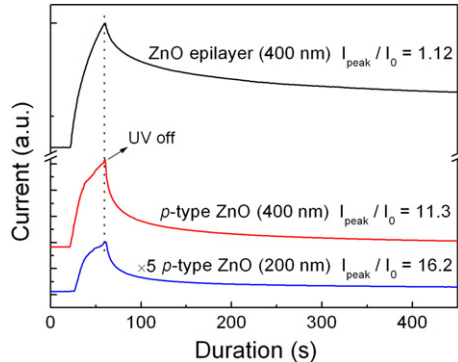


Fig. 1. Comparative UV photoconductivity of ZnO epilayer and p-type ZnO:N films with different thicknesses.

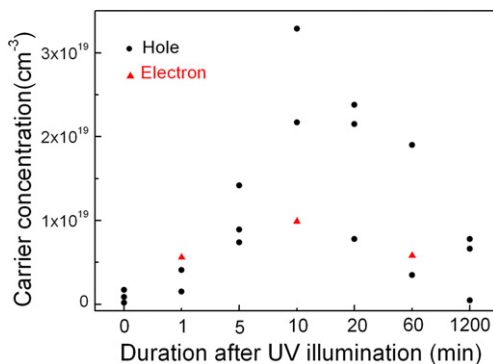


Fig. 2. Statistical results of Hall-effect measurements on ZnO:N films before and after UV illumination.

ductivity after UV illumination, showing an acceptable stability upon UV illumination.

Since the photoconductivity of a semiconductor is usually controlled by surface effect [21], the surface morphologies of ZnO epilayer and p-type ZnO:N were characterized by FE-SEM to better understand the observed UV photoconductivity. Fig. 3 compares the surface images, illustrating widely different morphologies. ZnO epilayer shows well epitaxial characteristic with little grain boundary. Whereas, ZnO:N film exhibits small crystalline grain with dense grain boundary, which is probably caused by the N-doping and the decreasing crystalline. In addition, the optimal ratio of Zn/O in the ZnO epilayer is not available for the ZnO:N due to a narrow window for the effective N-doping. The optimal growth pressure is also forbidden for the ZnO:N because a low growth pressure is required by the plasma generator. The polycrystalline surface of ZnO:N is, therefore, easily to be adsorbed.

Further evidence for the surface adsorption is provided by XPS. Fig. 4a illustrates C 1s narrow scan spectra of p-type ZnO:N. Surface scan spectrum reveals two peaks centered at 284.8 eV and 288.6 eV, which are attributed to C–O (or C–H) and C=O, respectively. After the surface

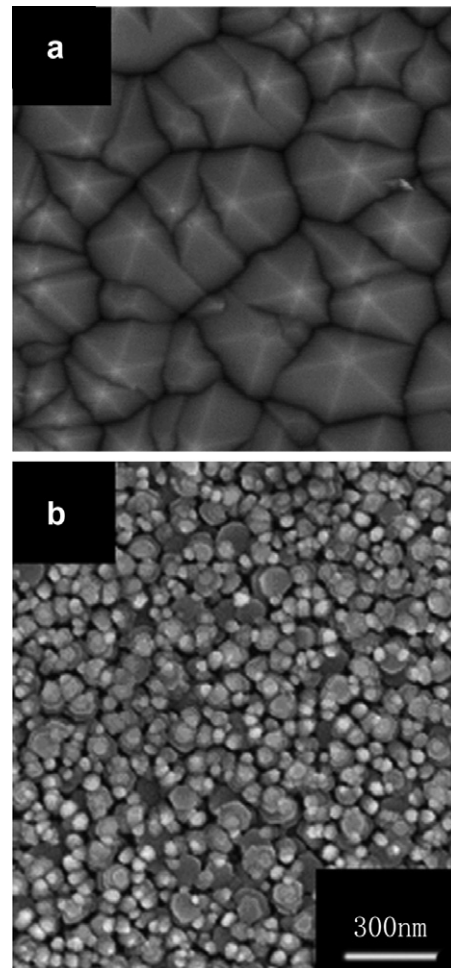


Fig. 3. FE-SEM surface images of ZnO epilayer (a) and p-type ZnO:N thin film (b).

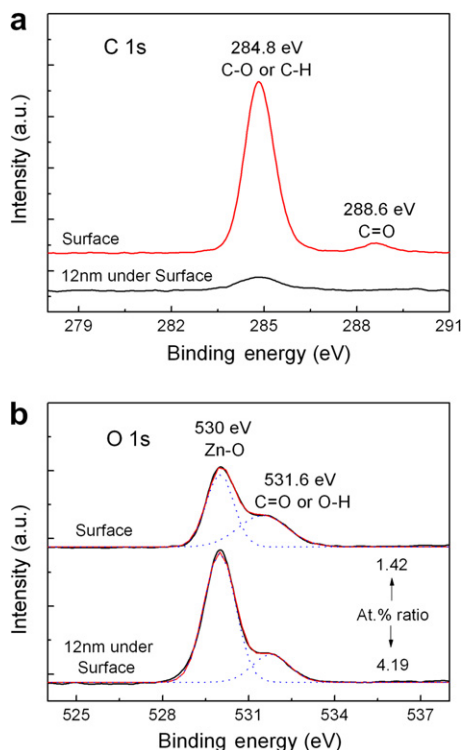


Fig. 4. C 1s (a) and O 1s (b) XPS narrow scan spectra for p-type ZnO:N film.

was etched by Ar ion bombardment, C 1s signal has been suppressed evidently, suggesting a strong surface adsorption of C and O. In addition, Fig. 4b illustrates O 1s narrow scan spectra. Both spectra reveals two peaks centered at 530 eV and 531.6 eV, which are attributed to Zn–O and C=O (or O–H), respectively. However, the ratio of these two chemical states increases from 1.42 to 4.19 after Ar ion bombardment, which again indicates a surface adsorption of C and O. The strong surface adsorption in ZnO:N film is believed to be the result of the small crystalline grain with dense grain boundary on the surface (see Fig. 3b). Note that similar XPS measurements on the ZnO epilayer reveal a weaker surface adsorption in comparison with the ZnO:N film (data not shown). This is due to its well epitaxial surface with little grain boundary (see Fig. 3a). Therefore, it is reasonable to infer that the observed comparative photoconductivity should be associated with the different surface morphologies and corresponding diverse surface adsorption behaviors.

Base on above-introduced analyses, a surface adsorption and photodesorption process in p-type ZnO:N is proposed tentatively, as illustrated in Fig. 5. In the absence of UV light, C and O are easily adsorbed on the surface of p-type ZnO:N film, forming C–O and C=O chemical complexes, as confirmed by XPS. These chemical complexes will take free holes to form positively charged surface state, leaving behind a depletion layer and built-in electrical field pointing from surface to inside. When the UV light is incident, electrons produced by the light absorption will be derived by the built-in electrical field to discharge the pos-

itively charged surface. Simultaneously, the C–O and C=O chemical complexes undergo a photodesorption process. Holes produced at the same time increase the conductivity of p-type ZnO:N film. The situation for the n-type ZnO epilayer is quite similar, except that the major carrier is electron instead. Because the surface adsorption effect is stronger for the ZnO:N film in comparison with the ZnO epilayer, a corresponding larger value of  $I_{\text{peak}}/I_0$  can be expected, especially for the 200-nm thin film with a larger ratio of surface state (see Fig. 1). In addition, the effect of non-equilibrium carrier on photoconductivity will be more significant in p-type material due to the deeper acceptor level, which will also result in a larger value of  $I_{\text{peak}}/I_0$ . After the UV light is cut off, C and O are adsorbed again to take the major carrier, forming charged surface states and decreasing the conductivity. This process occurs much faster in the ZnO:N film due to the small crystalline grain with dense grain boundary, which will lead to a faster decay of photoconductivity.

We now turn to the Hall-effect results of ZnO:N films after UV illumination, as summarized in Fig. 2. It is supposed that some electrons, bound to structural defects in ZnO:N, will also be activated after UV illumination and contribute to the conductivity. The unreasonably high (up to  $10^{19} \text{ cm}^{-3}$ ) and scattered hole concentrations, with occasional n-type signals, are thought to be the result of the competition between holes and electrons. Because a mixed-conduction could result in artificially high hole concentration but with low Hall mobility, which is exactly the present case. On the other hand, in the polycrystalline ZnO:N with dense grain boundary, the electric potential

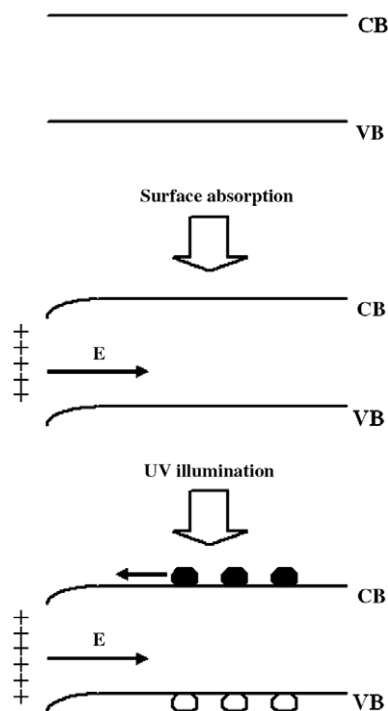


Fig. 5. Surface adsorption and photodesorption process for p-type ZnO:N film.

and flow current at the grain boundary could also lead to an ambiguous carrier type. We believe that the mixed-conduction effect, together with a polycrystalline nature, serves as the primary origins of the instability in p-type material currently [19,20].

#### 4. Conclusions

In summary, we have demonstrated comparative study on UV photoconductivity of p-type ZnO:N films and n-type ZnO epilayer. The surface adsorption and photodesorption process, combined with a competition between holes and electrons, in p-type ZnO:N is proposed, providing qualitative agreement with the observed behaviors. We hope this study will address the reproducibility and stability surrounding this material.

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