

Dynamical Properties of Hydrogen in ZnO:H Treated by H₂/Ar Plasma under Atmospheric Pressure

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1. Introduction

ZnO is a wide-band-gap semiconductor with many technological applications, including catalysis, gas sensing, and the fabrication of microelectronic devices [1-3]. The geometric, electronic, and defect surface structures play a role in many applications of ZnO [1,2]. Recently, Wang *et al.* reported that enhanced optoelectronic properties can be obtained by a H₂/Ar mixed plasma treatment due to thermal stability of H in ZnO nanorods [2]. Two hydrogen species, i.e., interstitial hydrogen (H_i) and substitutional H (H_O) at an O site are suggested to be favorable shallow donors in ZnO. To enhance the thermal stability of H in the samples, one might need to increase the concentration of H_O which has greater stability than H_i [2,3]. Thus, identification of H_O and understanding of its diffusional mechanism are still important issues to be solved.

Here we investigate dynamical properties of hydrogen adsorbed on ZnO surface (ZnO:H) by a H₂/Ar mixed plasma treatment. Electron spin resonance (ESR) measurement on temperature was made to identify occupied energy states of H in ZnO:H, the g-value of H being revealed to be 1.96. The dynamical properties of ZnO:H are discussed in view of conversion to hydrogen molecule by analyzing the spin-lattice relaxation time of ¹H nuclear magnetic resonance (NMR) spectroscopy.

2. Methods

Zinc acetate, (CH₃COO)₂Zn·2H₂O, supplied by Aldrich, was used for the sample synthesis. The ZnO polycrystalline sample was prepared by sol-gel method from a water soluble zinc acetate precursor following previous works [3], the dried mixture being calcined for 8 h at 673 K. The ZnO nanorods were treated by mixed H₂/Ar plasma at power of 300 W for 5 min using an atmospheric pressure plasma treater installed at Korea Multi-purpose Accelerator Complex (KOMAC). The trajectory profile as a function of depth was obtained using SRIM (stopping and range of ions in matter) simulation. ESR measurement was made at room temperature by using a X-band ESR spectrometer. The ¹H magic-angle spinning NMR measurements were made by using a 400-MHz ¹H pulsed NMR spectrometer with a spinning rate of 11 kHz in a temperature range of 200 K to 400 K.

3. Results and discussion

3.1 SRIM simulation

The SRIM simulation for the trajectory profile along the target depth for 10 eV H⁺ ions in ZnO (Fig. 1) shows an ununiform distribution of the protons. The simulation results show that most of H⁺ ions are adsorbed within the first ~2 nm of the surface. The radiation energy of 10 eV was assumed because the H dopants accumulate mostly at the top surface of the ZnO nanorods with the H₂/Ar plasma treatment [2]. In contrast, the H₂ plasma is relatively effective to distribute H into the ZnO nanorods, according to the previous report [2].

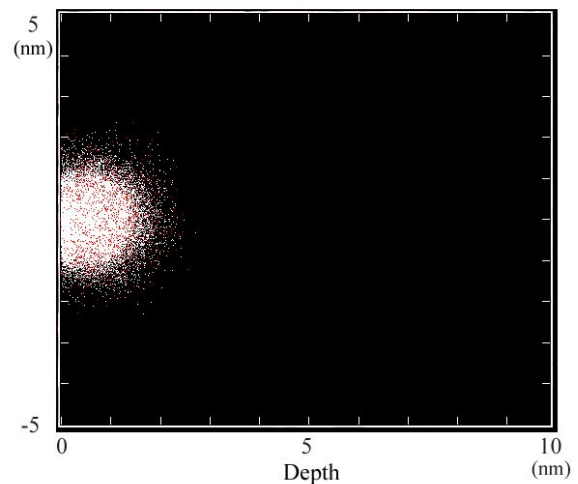


Fig. 1. SRIM simulation of projectory profile of incident H⁺ ions along target depth in ZnO.

3.2 ESR spectra

In Fig. 2, the two ESR peaks at g=1.96 and g=2.003 were observed in ZnO:H, whereas two weak peaks centered at g=1.96 and g=2.003 were observed in ZnO. No resonance shifts of the two peaks upon temperature were observed in both ZnO and ZnO:H. It was previously reported that the H_O is thermally stable up to ~ 773 K, whereas H_i diffuses out above ~ 423 K [3]. The g=1.96 signal arises from hydrogen shallow donors, suggesting both H_i and H_O can be incorporated in ZnO [4].

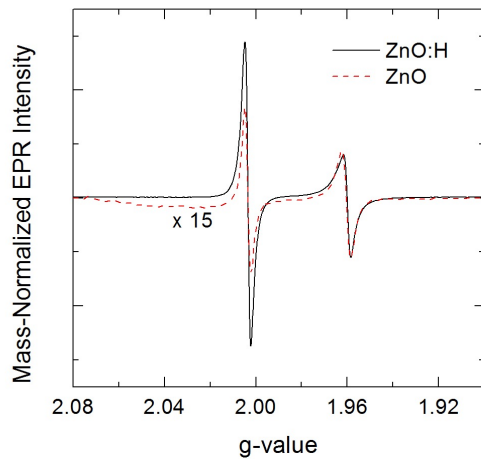


Fig. 2. Mass-normalized ESR spectra for ZnO and ZnO:H measured at room temperature. For comparison, the spectrum of ZnO was magnified by 15 times. Two ESR peaks at $g=2.003$ and $g=1.96$ are observed in both ZnO and ZnO:H, but the peaks in ZnO are very weak compared to those of ZnO:H.

The origin of the ESR peak centered at $g=2.003$ is still unclear because similar g -values of V_{Zn} and V_O make the assignment of the peaks difficult. Recently, Gehlhoff *et al.* demonstrated that the peak cannot arise from V_{Zn} -H pair defects in nano-powder sample by their theoretical study [5]. It is to be noted that in only ZnO single crystal but not the powder-like nanocrystal the peak at $g \sim 2.003$ was attributed to the V_{Zn} by previous works [5]. We find from the ESR measurement on temperature that the activation energies of the peak of V_O ($g=2.003$) are small, indicating a shallow level defect. Previous works, however, reported that since the

oxygen vacancy with a single trapped electron (V_O^+) is a metastable defect located deep in the bandgap, it thus can only be observed by illumination of light. On the other hand, the interaction between delocalized π -electrons of carbon-inherited spin species and V_O^+ makes transition from deep level defect to shallow one. In our samples, the carbon as impurities can be introduced due to synthesis at relatively low temperature. Therefore, we attribute the peak centered at $g=2.003$ to V_O^+ defect centers interacting with π -electrons of carbon [6].

4. Conclusions

We have investigated the diffusional properties of hydrogen adsorbed on ZnO surface (ZnO:H) by a H_2/Ar mixed plasma treatment installed at KOMAC. Electron spin resonance measurement identified occupied energy states of H in ZnO:H, the g -value of H being revealed to be 1.96. In further work, the proton dynamics of ZnO:H would be discussed in view of conversion to hydrogen molecule by analyzing the spin-lattice relaxation time of 1H nuclear magnetic resonance spectroscopy.

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