Enhanced conductivity of zinc oxide thin films by ion implantation of hydrogen atoms

Shigemi Kohiki,[a] Mikihiko Nishitani, Takahiro Wada, and Takashi Hirao
Central Research Laboratories, Matsushita Electric Industrial Co. Ltd., 3-4, Hikaridai, Seika, Souraku, Kyoto 619-02, Japan

(Received 29 November 1993; accepted for publication 4 March 1994)

Enhancement of the conductivity of zinc oxide through doping with hydrogen atoms was examined by using ion implantation of highly resistive thin films deposited by rf magnetron sputtering at room temperature. With a doping of 1×10^{17} atoms cm^{-2}, the conductivity after annealing at 200 °C in an N_2 atmosphere at 1 atm rose from the initial $1\times10^{-7}\ \Omega^{-1}\,cm^{-1}$ to $5.5\times10^{2}\ \Omega^{-1}\,cm^{-1}$.

Zinc oxide (ZnO) in the form of thin film is a promising material for optoelectronic applications. It is well known that ZnO films doped with the group III elements (In, Ga, Al, and B)[1] exhibit good transparency and conducting properties. Recent experiments on highly resistive ZnO films doped with Ga, Al, and B atoms by ion implantation clearly show that impurities of Ga^{3+}, Al^{3+}, and B^{3+} form a monovalent and shallow impurity state ($E=51$ meV) by substituting for Zn^{2+} in the crystal. The effectiveness of the enhancement in conductivity (Ga>Al>B) is explained by the electronegativity of the dopant.[2]

Hydrogen atoms, expected to occupy the interstitial site in the ZnO crystal from a consideration of the Bohr radius, are promising dopants acting as donors. It has been reported that the conductivities of the films grown at room temperature by Ar ion beam sputtering of a ZnO target with hydrogen gas[3] and hydrogen ions[4] attain values of 4×10^{2} and $2\times10^{2}\ \Omega^{-1}\,cm^{-1}$, respectively.

In this letter we report the doping effects of hydrogen atoms for highly resistive ZnO films. The films were deposited by rf magnetron sputtering at room temperature (RT). Sputtering conditions are listed in Table I. A strong preferred orientation of the c-axis normal to the surface was observed by x-ray diffraction of the films. The conductivity and conduction type of the films were measured by the van der Pauw method and Hall measurement, respectively, using electrodes formed by the deposition of NiCr (200 Å) followed by Au (1500 Å).

The as-deposited films were highly resistive ($1\times10^{-7}\ \Omega^{-1}\,cm^{-1}$). Although ZnO is considered to contain both singly ionized Zn at interstitial sites, $Zn_i^{\cdot}$, and oxygen vacancies, $V_O^{\cdot}$, which are responsible for the n-type conduction, the issue is still a subject of debate. The sum of the concentrations of acceptor type defects $[V'_{Zn}]$ and $[O'_i]$ must be the same as that of donor type defects $[Zn_i^{\cdot}]$ and $[V_O^{\cdot}]$ to satisfy the principle of electrical neutrality for the highly resistive as-deposited films.

The defects can exist in the form of a neutral, singly, or doubly ionized state.[5] Excess zinc interstitials can transfer one or two electrons into the conduction band, forming $Zn_i^{\cdot}$ or $Zn_i^{\cdot\cdot}$, respectively.[5] An appropriate electroneutrality condition for Zn sublattice might be expressed as follows:

$$[V'_{Zn}]+2[V''_{Zn}]+n=[Zn_i^{\cdot}]+2[Zn_i^{\cdot\cdot}]+p.$$

Here, n and p indicate the charge carriers of n and p types. High resistivity is needed to identify the effect of dopant on conductivity of the films.

The films were doped with hydrogen atoms using an ion implantation technique. H^{+} ions accelerated to an energy of 100 keV were implanted into the films with doses of 1×10^{17}, 1×10^{16}, and 1×10^{15} ions cm^{-2} by using a 400 keV-ion-implanter (Ion Engineering Center Co., Osaka, Japan). The ion current density was below 2×10^{-8} A cm^{-2} and the sample temperature did not exceed 100 °C during the implantation.

The samples doped with 1×10^{17} ions cm^{-2} were pale yellow but those doped with 1×10^{16} ions cm^{-2} or less were visually colorless after the implantation. The implanted films were subjected to post-ion-bombardment annealing at 200 °C in an atomspheric pressure of N_2 for 1–4 h for the elemental diffusion and the recovery of ion-induced defects. The surfaces of the implanted films, however, were not etched. The yellow color disappeared after annealing for 4 h.

The conductivities of the films annealed at 200 °C in an N_2 atmosphere at 1 atm are shown in Fig. 1. The annealing has little effect on the conductivity of samples A and B which are heavily implanted with hydrogen. The effect of doping, however, is obvious for these two samples. The conductivity of the films increased with increasing implantation dose. The increments of the conductivity of the samples A and B by implantation amount to approximately 10^{10} and 10^{8}, respectively. The conductivity of sample A (dose of 1×10^{17} ions cm^{-2}) was $5.5\times10^{2}\ \Omega^{-1}\,cm^{-1}$, which is the highest value yet reported for hydrogen-doped ZnO films. The mobility and carrier concentration of sample A were $9.5\ cm^{2}\,V\,s^{-1}$ and $3.3\times10^{21}\ cm^{-3}$, respectively. Doses greater than 1×10^{16} ions cm^{-2} are necessary to reproducibly obtain high conductivities.

TABLE I. Conditions for the deposition of undoped ZnO films.

Target	ZnO
Sputtering gas	Ar 90%+O_2 10%
Pressure	8×10^{-3} Torr
Rf power	1000 W
Substrate	Corning 7059 glass
Substrate temp.	Room temperature
Deposition rate	250 Å/min
Film thickness	2×10^{4} Å

[a]Present address: Kochi National College of Technology, 200-1, Monobe, Nangoku, Kochi 783, Japan. Author to whom correspondence should be addressed.

 0003-6951/94/64(21)/2876/3/$6.00 © 1994 American Institute of Physics

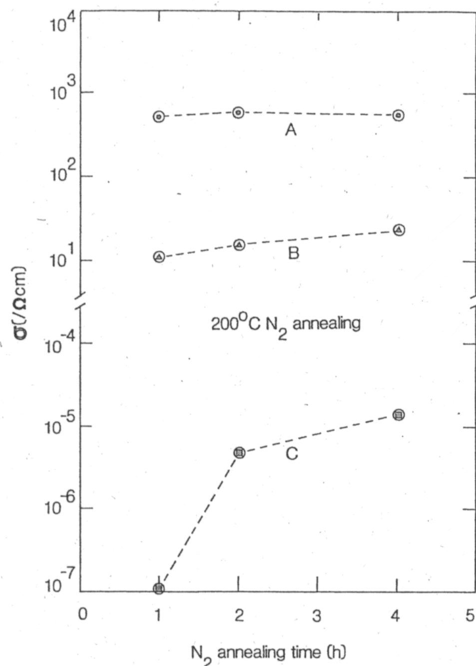

FIG. 1. Conductivity vs annealing time at 200 °C of the ZnO films doped with hydrogen atoms (A: 1×10^{17}, B: 1×10^{16}, and C: 1×10^{15} ions cm^2).

The annealing greatly affects the conductivity of a film with low implantation dosage of 1×10^{15} ions cm^{-2}. Although the conductivity of sample C increased by 2 orders of magnitude after 4 h of annealing, the resultant conductivity of $10^{-7}\ \Omega^{-1}\ cm^{-1}$ is far below the value obtained by heavily doping as in samples A and B. Doping in excess of the initial defect concentration is indispensable for reliable control of the electric properties of the films.

Since the Bohr radius of a hydrogen atom is very small (0.52 Å) and the activation energy for diffusion is 0.91 eV in ZnO,[6] doped hydrogen atoms jump from one interstitial site to the next and form OH ions in the form of $(O_O H_i)^{\cdot}$, which have small ionization energy.[7] Here, O_O, H_i, and $\cdot$ represent the O ion on oxygen lattice site, H atom in interstitial site, and singly ionized donor, respectively.

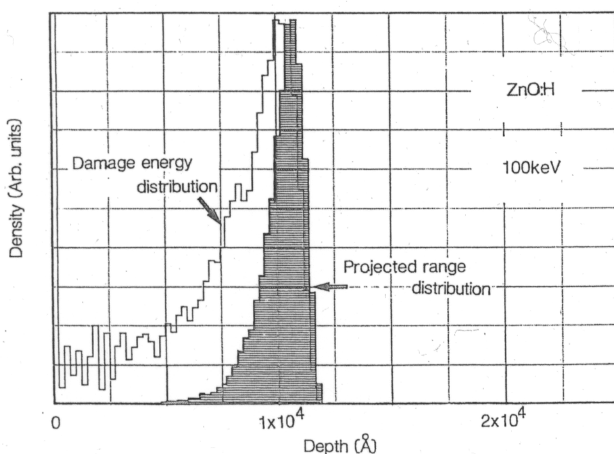

FIG. 2. Simulated depth profiles of implanted hydrogen atoms and damaged layers of ZnO.

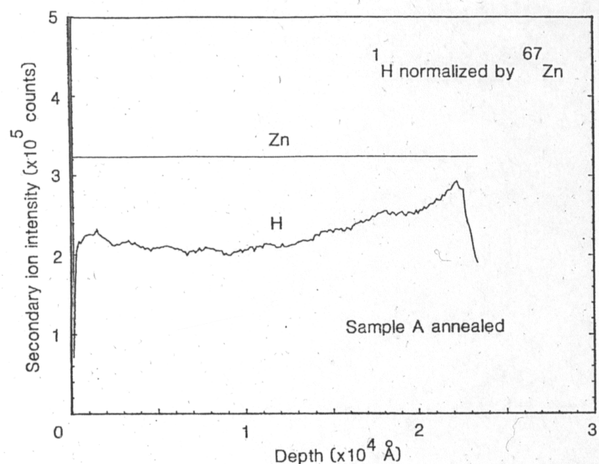

FIG. 3. Depth profile by SIMS of the ZnO:H film (A) annealed for 4 h.

Figure 2 shows the depth profiles of implanted hydrogen atoms and the damaged layer simulated by the TRIM code calculation based on the Monte Carlo method.[8] The calculation assumed that the ions were injected vertically into the surface of the polycrystalline ZnO target without sputtering effects (surface etching and roughing) or diffusion (thermal diffusion and grain boundary diffusion). The projected range of the atoms was approximately 1×10^4 Å.

Figure 3 shows the depth profile of hydrogen atoms in the annealed sample by secondary ion mass spectrometry (SIMS). A CAMECA IMS-4f was used for the SIMS measurement with primary O_2^+ ions accelerated at 4.0 keV. The primary ion current was 50 nA/0.15 mm square. Positive ions $^1H^+$ and $^{67}Zn^+$ were detected but no peak was observed in the interior of the film. Implanted hydrogen atoms diffused and segregated at the interface between the ZnO film and glass substrate. The difference in the depth profiles expected from the TRIM calculation and the SIMS measurement must be due to the out-diffusion of implanted hydrogen atoms.

Hydrogen treatment as well as doping with Al, Ga, and In increases the intensity of the $g=1.96$ signal of the electron spin-resonance measurement.[9] The $g=1.96$ signal is due to free electrons in the conduction band e_C rather than $V_O^{\cdot}$.[9] Ion implantation with high concentration of hydrogen ($>1\times10^{16}$ atoms cm^{-2}) must result in the overlap of the donor band and the conduction band.

Doses of hydrogen atoms more than 1×10^{16} ions cm^{-2} are necessary to reproducibly obtain large conductivities. Doped hydrogen atoms form OH ions which act as donors in the ZnO crystal and enhance the conductivity. The conductivity of the film with the doses of 1×10^{17} ions cm^{-2} was $5.5\times10^2\ \Omega^{-1}\ cm^{-1}$, which is the highest value yet reported for ZnO films doped with hydrogen.

A part of this work was supported by the New Energy and Industrial Technology Development Organization as part of the New Sunshine Program under the Ministry of International Trade and Industry. The authors thank Dr. T. Karasawa

for a critical reading of the manuscript, S. Yoshikawa for assistance with the SIMS analyses, Dr. T. Nitta for encouragement, and the staff of Ion Engineering Center Co. for assistance with ion implantation.

[1] T. Minami, Oyobuturi **61**, 1255 (1992) (in Japanese).
[2] S. Kohiki, M. Nishitani, and T. Wada, J. Appl. Phys. **75**, 2069 (1994).
[3] S. Kohiki, M. Nishitani, and T. Wada (unpublished).
[4] A. Valentini, F. Quaranta, M. Penza, and F. R. Rizzi, J. Appl. Phys. **73**, 1143 (1993).
[5] G. Neumann, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, p. 154, and references therein.
[6] D. G. Thomas and J. J. Lander, J. Chem. Phys. **25**, 1136 (1956).
[7] G. Neumann, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. 7, p. 279, and references therein.
[8] J. P. Biersack, L. G. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).
[9] G. Neumann, in *Current Topics in Materials Science*, edited by E. Kaldis (North-Holland, Amsterdam, 1981), Vol. **7**, p. 269, and references therein.