Enhanced electrical conductivity of zinc oxide thin films by ion implantation of gallium, aluminum, and boron atoms

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Effect of ion implantation on the conductivity of zinc oxide was examined by using highly resistive zinc oxide thin films deposited by rf magnetron sputtering at room temperature to reduce the effect of oxygen vacancies. With the doping by 1×10^{17} atoms/cm^2 gallium the conductivity is $1.0\times10^3/\Omega$ cm for as-implanted film and it increases up to $3.7\times10^3/\Omega$ cm, the highest conductivity reported for zinc oxide films, with raising the annealing temperature in either a nitrogen or oxygen atmosphere. The conductivity of aluminum-doped films is slightly lower than those of gallium-doped films. Among the elements gallium, aluminum, and boron, gallium is the most effective in enhancing the conductivity and boron is the least. The order of the effectiveness is explained by the electronegativity of the dopants.

I. INTRODUCTION

Thin films of doped zinc oxide (ZnO) are a promising material for the field of display and photovoltaic devices because of their high transparency and electrical conductivity. Various techniques such as vacuum evaporation, reactive sputtering, rf magnetron sputtering, ionized cluster beam deposition, spray pyrolysis, and chemical vapor deposition have been used to fabricate thin films of ZnO. An rf magnetron sputtering deposition has been one of the favorable methods since it is easy to control the deposition parameters.[1] A thin film of nondoped ZnO deposited at room temperature (RT) has low conductivity but the films doped with the group III elements (In, Ga, Al, and B)[2] exhibit high conductivity. A target for the deposition of aluminum-doped ZnO (ZnO:Al) consists of ZnO and Al_2O_3. If the composition of a ZnO:Al film deposited by rf sputtering was the same as that of the target, the film should be highly resistive. However, the actual film is conductive because of the existence of various lattice vacancies. Therefore, ZnO film with high resistivity is needed to identify the effects of dopants on conductivity of the films.

In this article we report doping effects of Ga, Al, and B atoms for highly resistive nondoped ZnO films. Atoms of Ga, Al, and B are doped using an ion implantation technique which is suitable to study the doping effects. Ga and B are the most and least effective dopants among the implanted species, respectively. The trend in the degree of conductivity enhancement ($Ga > Al \gg B$) can be explained by the electronegativity of these atoms.

II. EXPERIMENT

The ion implantation technique which is well established in semiconductor technology was employed to dope foreign (Ga, Al, and B) atoms into nondoped ZnO thin films deposited by rf magnetron sputtering. Sputtering conditions are listed in Table I.

A large preferred *c*-axis orientation was observed by x-ray diffraction of as-deposited, as-implanted, and annealed films as shown in Fig. 1. The *c*-axis lattice constant estimated from the (002) reflection was 5.25 Å for the as-deposited film and that for the implanted-annealed films was 5.21 Å. The *c*-axis lattice constant of the as-deposited film is larger than that of the single crystal (5.213 Å).[3] After annealing, however, implanted films have the same *c*-axis lattice constant as the single crystal. The conductivity and conduction type of the films were measured by the conventional 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 film exhibited the small conductivity of approximately $1\times10^{-7}/\Omega$ cm. This low conductivity and large *c*-axis lattice constant may be due to a high oxygen content in the as-deposited films. It is generally considered that the films deposited by rf sputtering are more oxygen rich than the single crystals.[4]

Ga^+, Al^+, and B^+ ions accelerated at energies of 2000, 1000, and 500 keV, respectively, were implanted into the films with the doses of 1×10^{17}, 1×10^{16}, and 1×10^{15} ions/cm^2 using an 8 MeV-Ion Implanter installed at the 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, but the color of the films was changed from colorless to yellowish brown by the implantation. The yellowish-brown color was deeper for the samples implanted with higher doses even after annealing in a 1 atm N_2 atmosphere for 4 h as shown in Fig. 2. The samples doped with 1×10^{17} ions/cm^2 were visually pale yellow but those doped with 1×10^{16} ions/cm^2 were colorless after the annealing. The implanted films were subjected to post-ion-bombardment

TABLE I. Conditions of the deposition of nondoped 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

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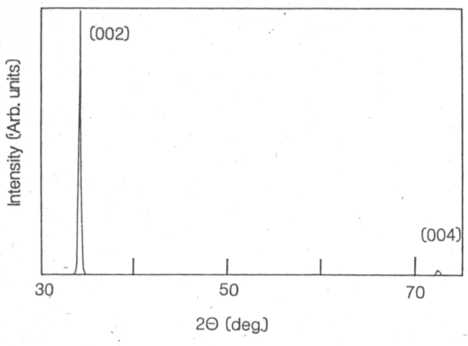


FIG. 1. X-ray diffraction pattern with a Cu K α x-ray of the film of ZnO:Ga (1×10^{17} ions/cm^2) annealed at 400 °C for 4 h in N_2.

annealing for the elemental diffusion and the recovery of ion-induced defects, but the surfaces of the implanted films were not etched.

Depth profiles of implanted Ga, Al, and B atoms and the damaged layers were simulated by the TRIM code calculation for the ions injected vertically into the surface of a polycrystalline ZnO target without sputtering effects (surface etching and roughening) and diffusion (thermal diffusion and grain boundary diffusion). The TRIM calculation is based on the Monte Carlo method.[5] The projected range (Rp) of the atoms was approximately $(1.1–1.2)\times10^4$ Å as shown in Figs. 3(a)–3(c).

Rp's obtained by the simulation agree fairly well with the result of secondary ion mass spectrometry (SIMS) measurements for the films implanted with Ga, Al, and B at energies ranging from 500 to 2000 keV. 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^2. Positive ions (^{11}B, ^{27}Al, ^{69}Ga, ^{16}O, ^{67}Zn) were detected and the maxima in the depth profiles of the implanted atoms were taken as the experimental Rp. Actual Rp's of Ga, Al, and B implanted at 2000, 1000, and 500 keV were 1×10^4 Å as shown in Fig. 4. The differences

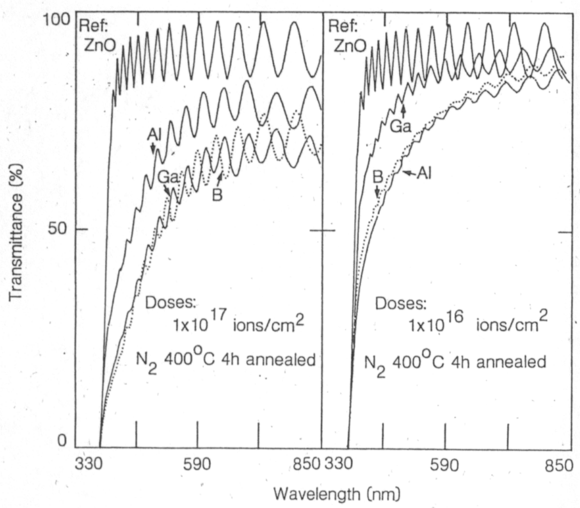


FIG. 2. Optical spectra in ultraviolet and visible region of the doped and nondoped ZnO films.

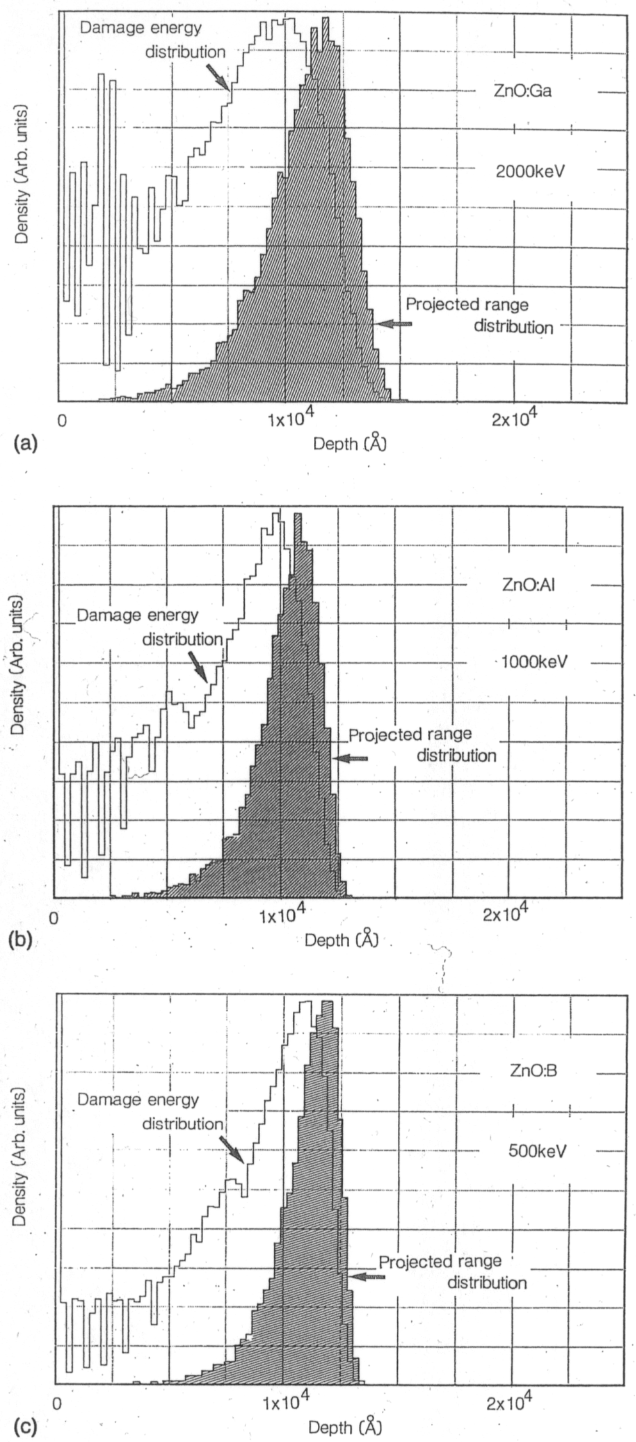


FIG. 3. Simulated depth profiles of implanted atoms with damaged layers of ZnO. (a)–(c) are for Ga at 2000 keV, Al at 1000 keV, and B at 500 keV, respectively.

in values between the simulations and SIMS measurements are ascribable to the sputtering of the film surface during the ion implantation.

III. RESULTS AND DISCUSSION

It has been believed that ZnO contains both singly ionized Zn at interstitial sites, $Zn_i^{\cdot}$ and oxygen vacancies, $V_O^{\cdot}$, which are responsible for the *n*-type conduction, but there has been no evidence of the existence of these defects

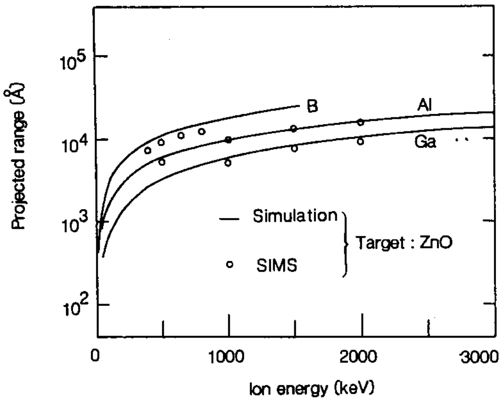


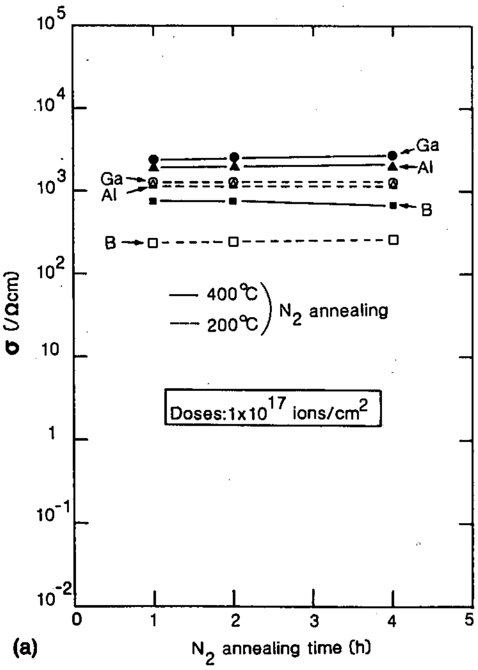
FIG. 4. Comparison of the projected range vs the ion energy obtained by simulation and experiment.

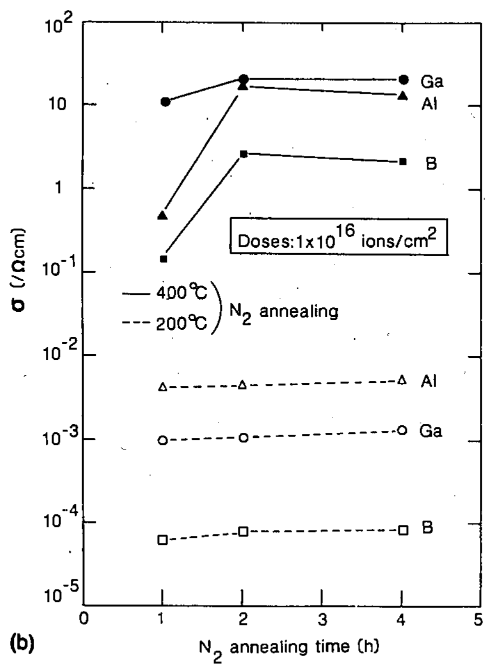
TABLE II. Conductivity of as-implanted ZnO films $(\Omega\ \text{cm})^{-1}$.

Doses (ions/cm^2)	Ga	Al	B
1×10^{17}	1.0×10^{3}	9.3×10^{2}	9.3×10^{1}
1×10^{16}	3.1×10^{-6}	1.8×10^{-3}	1.6×10^{-5}
1×10^{15}	2.2×10^{-6}	1.1×10^{-3}	5.2×10^{-7}

in ZnO films deposited at RT by rf magnetron sputtering. In this experiment we used highly resistive nondoped ZnO films $(1\times10^{-7}/\Omega\ \text{cm})$. Concentration of defects V'_{Zn} and O'_i must be the same to satisfy the principle of electrical neutrality.

It is well known that doping by foreign atoms in excess of the number of defects is indispensable for the reliable





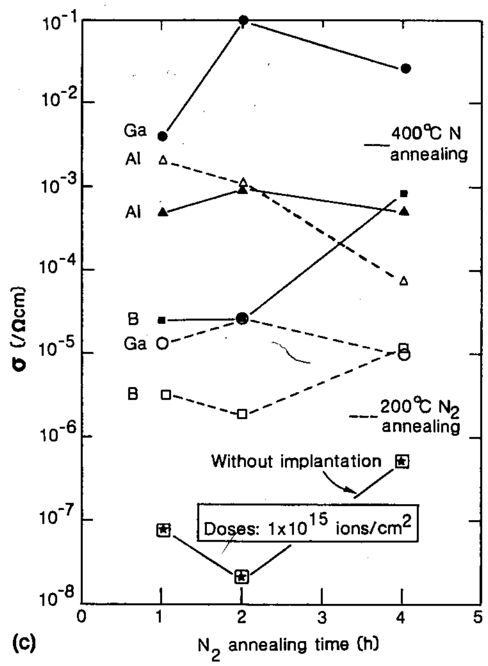


FIG. 5. Conductivity vs annealing time at 400 and 200 °C for the ZnO films doped with Ga, Al, and B. (a)–(c) are for the films with doses 1×10^{17}, 1×10^{16}, and 1×10^{15} ions/cm^2, respectively.

TABLE III. Atomic radii for tetrahedral coordination and electronegativities of the atoms.

Atoms	Atomic radii (Å)	Electronegativity
B	0.853	2.00
Al	1.230	1.18
Ga	1.225	1.13
Zn	1.225	0.99

TABLE IV. Conductivity of the N_2 or O_2 annealed ZnO films (doped Ga, and Al with 1×10^{17} ions/cm^2).

Annealing conditions		Conductivity ($\times10^3/\Omega$ cm)	
Atmosphere	Temperature	Ga doped	Al doped
N_2	200 °C	1.25	1.17
O_2	300 °C	1.55	1.21
N_2	400 °C	2.62	1.83
O_2	500 °C	3.74	2.38

control of the electric properties of the crystal. Conductivities of the as-implanted films are listed in Table II, and those of films annealed in 1 atm N_2 are shown in Figs. 5(a)–5(c). The dosage of 1×10^{17} ions/cm^2 or more is needed to obtain high conductivity for both as-implanted and annealed ZnO films. The conductivity of the doped ZnO films increased with increasing dosage of a certain atom and a certain annealing condition. The conductivity of the films annealed at 400 °C was larger than that of the films annealed at 200 °C for a certain dopant atom and a certain dosage. These are obviously the effects of doping by foreign atoms, and not by the defects ($Zn_i^{\cdot}$ and $V_O^{\cdot}$) in the crystal.

From a consideration of the atomic radii for tetrahedral coordination (Table III),[6] it is expected that Ga^{3+}, Al^{3+}, and B^{3+} act as donor atoms in ZnO by substituting for Zn, and the most preferable dopant is Ga because the lattice distortion is the smallest when Zn is substituted by Ga. The doping effect of Ga, Al, and B atoms can be well understood in the context of a simple spherical model of a monovalent impurity state. In the model the energy is given by the following equation:

$$E=(m^*/m)(Ry/\epsilon^2).$$

Here, m^*/m is the effective mass (0.26) and ϵ is the static dielectric constant (8.3) (Ref. 3), which gives the energy E of 0.051 eV. Therefore, the monovalent impurities Ga^{3+}, Al^{3+}, and B^{3+} substituting for Zn^{2+} form a shallow impurity state in a ZnO crystal. At the dose level of more than 1×10^{17} ions/cm^2, implanted Ga, Al, and B atoms deliver an excess valence electron as donor into the lattice through the overlap of the impurity band with the conduction band.[7]

Ga was the most efficient dopant for the enhancement of conductivity of the ZnO films. The Ga-doped films showed the highest conductivity in almost all cases as shown in Figs. 5(a)–5(c). Contrary to Ga, the B-doped films showed the lowest conductivity in all cases. The conductivities of the films annealed in a N_2 or O_2 atmosphere are listed in Table IV. The Ga-doped films showed slightly higher conductivity than the Al-doped films at each temperature. With the dosage of 1×10^{17} ions/cm^2 and annealing at 200 °C for 4 h, the carrier concentrations of the films doped with Ga, Al, and B were 6.71×10^{20}, 4.37×10^{20}, and 1.18×10^{20} electrons/cm^3, respectively. The doping effect was the highest for Ga, and the lowest for B.

This trend of the doping effect, i.e., the highest conductivity is obtained with the Ga-doped film and the lowest one is obtained with the B-doped film, can be predicted by the electronegativity of the dopant atoms, as listed in Table III.[6] The smallest electronegativity is for Zn and the largest one is for B. The difference in electronegativity is the smallest between Zn and Ga, but the largest between Zn and B. The dopant atom B, substituted for Zn, strongly attracts the electrons in the conduction band around its position in the lattice, but the localization effect of conduction electrons by Ga is smaller than those by B and Al, therefore the highest doping effects must be realized by the Ga ion implantation for highly resistive ZnO film.

IV. CONCLUSION

Doses of more than 1×10^{17} ions/cm^2 Ga, Al, and B atoms are necessary to obtain high conductivity of the ZnO films. Ga^{3+}, Al^{3+}, and B^{3+} substitute for Zn^{2+} in the ZnO film and they form a shallow (E=0.051 eV) monovalent donor level. The doping of Ga is the most effective in enhancing the conductivity of a ZnO film, and the doping of B is the least. The trend of the doping effect (Ga > Al $\gg$ B) can be explained by the electronegativities of the elements.

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