Zubiaga, Asier; Tuomisto, Filip; Coleman, Victoria; Tan, Hoe H.; Jagadish, Chennupati; Koike, Kazuto; Sasa, Shigehiko; Inoue, Masataka; Yano, Mitsuaki

Mechanisms of electrical isolation in O+-irradiated ZnO

Published in:
Physical Review B

DOI:
10.1103/PhysRevB.78.035125

Published: 01/07/2008

Please cite the original version:
https://doi.org/10.1103/PhysRevB.78.035125
Mechanisms of electrical isolation in O⁺-irradiated ZnO

A. Zubiaga* and F. Tuomisto
Department of Engineering Physics, Helsinki University of Technology, Espoo 02015, Finland

V. A. Coleman, H. H. Tan, and C. Jagadish
Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia

K. Koike, S. Sasa, M. Inoue, and M. Yano
Nanomaterials Microdevices Research Center, Osaka Institute of Technology, Osaka 553-8585, Japan

(Received 24 April 2008; revised manuscript received 2 June 2008; published 25 July 2008)

We have applied positron annihilation spectroscopy combined with sheet resistance measurements to study the electrical isolation of thin ZnO layers irradiated with 2 MeV O⁺ ions at various fluences. Our results indicate that Zn vacancies, the dominant defects detected by positrons, are produced in the irradiation at a relatively low rate of about 2000 cm⁻¹ when the ion fluence is at most 10¹⁵ cm⁻² and that vacancy clusters are created at higher fluences. The Zn vacancies introduced in the irradiation act as dominant compensating centers and cause the electrical isolation, while the results suggest that the vacancy clusters are electrically inactive.

DOI: 10.1103/PhysRevB.78.035125 PACS number(s): 73.61.Ga, 78.70.Bj, 73.50.−h, 72.80.Ey

INTRODUCTION

ZnO is a II–VI compound semiconductor with a large band gap (3.37 eV at room temperature) that makes it a suitable material for the development of blue-ultraviolet solid-state light emitters. Its large exciton binding energy makes it a particularly efficient emitter at room temperature. The recent improvements of the growth processes have enabled the production of good quality bulk samples and thin films. More challenging is to understand the origin of the defects present in the as-grown material and how dopants are incorporated. Typically as-grown nominally undoped ZnO has a high concentration of shallow donors that make it p type, but it has been found to be difficult to obtain samples with stable p-type conductivity.

The electrical and optical properties of ZnO have been shown to be more resistant to deterioration upon particle irradiation than those of its “rival,” GaN. In addition, ZnO remains crystalline until high irradiation fluences with heavy ions. These properties are most likely related to the strong dynamic annealing processes observed during the irradiation. The study of electrical isolation processes can give information about the structure of electrically active defects. Further, this kind of study can provide more insights into the structure and the behavior of defects that could allow the growth or processing by ion implantation of stable p-type material.

Positron annihilation studies have shown that Zn vacancies are created in electron irradiation of ZnO and that they compensate n-type doping. Their introduction rate has been measured to be markedly lower than for Ga vacancies in GaN, which points to the origin of the radiation hardness of the material. In addition, clustering of vacancy defects has been observed in ion-implanted ZnO. The interpretations presented in the above-mentioned works have been challenged in some reports (see, e.g., Ref. 16), but the data presented in this work reinforce the validity of the analyses in Refs. 9 and 17.

In this work we have combined positron annihilation spectroscopy with sheet resistance measurements in order to study the mechanisms of electrical isolation in Al-doped ZnO layers irradiated with 2 MeV O⁺ ions to various fluences.

EXPERIMENT

The ZnO layers were grown over a-sapphire by plasma assisted molecular-beam epitaxy (MBE) at Osaka Institute of Technology. Prior to irradiation, undoped samples had free-carrier mobilities of 79 cm²/V s from room-temperature Hall measurements and a sheet resistance $R_\text{s} \sim 1 \text{kΩ/sq}$ corresponding to a free-electron concentration of about $5 \times 10^{17}$ cm⁻³. Samples doped with Al at three different concentrations ($2 \times 10^{18}$, $5 \times 10^{18}$, and $10^{19}$ cm⁻³) had similar free-carrier mobilities. The samples were bombarded in a 1.7 MV tandem accelerator (NEC, 5SDH-4) with 2 MeV O⁺ ions at room temperature to various fluences up to $10^{17}$ cm⁻². The maximum damage peak and the O ions are placed within the sapphire substrate. To monitor electrical isolation in situ, samples were cut into $\sim 3.5$ mm² pieces, and In-Ga Ohmic contacts were prepared on opposite sides of each sample. Positron experiments were performed at room temperature with a monoenergetic positron beam. The implantation energy of the positrons was varied in the 0–38 keV energy range, and the Doppler broadening of the annihilation radiation was detected with two Ge detectors with an energy resolution of 1.24 keV at 511 keV. The data were analyzed using the conventional S and W parameters, defined as the fractions of counts in the central ($S$, $|E_\gamma - 511\text{ keV}| \leq 0.8$ keV) and the “wing” ($W$, $2.9$ keV $\leq |E_\gamma - 511\text{ keV}| \leq 7.4$ keV) parts of the annihilation line. More information about the experimental setup can be found elsewhere.

RESULTS AND DISCUSSION

The main results of the Doppler broadening experiments are collected in Figs. 1 and 2. Figure 1 shows the conven-
The positron diffusion lengths in the samples have been estimated fitting simultaneously the \( S \) and \( W \) parameters with \textsc{vepfit}.\textsuperscript{24} Values range between 15 and 20 nm for the positrons that annihilate in the implanted layer and above 200 nm for positrons the annihilate in the substrate. Samples that have not been irradiated have slightly longer diffusion length (20–30 nm). These values are typical of ZnO layers with a Zn vacancy concentration \([V_{\text{Zn}}]=10^{17} \text{ cm}^{-3}\),\textsuperscript{22,25} and they are much smaller than the measured layer thickness. Hence the diffusion of positrons can be neglected. The thickness of the layers can be estimated from two times the mean penetration depth at the point where positrons start to annihilate in the substrate.\textsuperscript{24} Values range between 600 and 850 nm, in good accordance with the nominal values.

Figure 2 presents the \((S, W)\) points measured in the ZnO layers, normalized to the values obtained in a ZnO reference sample (Ref. 17). The values for the Zn vacancy is taken from the same work and the effect due to having detectors with different resolutions have been taken into account.

Projected ion ranges calculated with Monte Carlo simulations (TRIM code).\textsuperscript{23}

As the \((S, W)\) values measured in the samples irradiated to a fluence of \(10^{17} \text{ cm}^{-2}\) coincide with the characteristic value in a ZnO reference sample (Ref. 17).

Projected ion ranges calculated with Monte Carlo simulations (TRIM code).\textsuperscript{23}

As the \((S, W)\) values measured in the samples irradiated to a fluence of \(10^{17} \text{ cm}^{-2}\) coincide with the characteristic val-

\[
\begin{align*}
\text{FIG. 1.} & \quad W \text{ and } S \text{ parameters versus the implantation energy. An undoped sample, two } O^+\text{-irradiated undoped samples (10}^{15} \text{ and }10^{17} \text{ cm}^{-2} \text{ fluences), an } [Al]=10^{19} \text{ cm}^{-3} \text{ doped sample, and an Al-} \\
& \quad \text{doped ([Al]}=10^{19} \text{ cm}^{-3}) \text{ and } O^+\text{-irradiated sample have been shown for comparison. Annihilation parameters have been normal-} \\
& \quad \text{ized to value in a ZnO reference sample (Ref. 17).}
\end{align*}
\]

![Graph showing \((S, W)\) parameters versus the implantation energy.](image-url)
The sheet resistance measurements presented above can correlate negatively with the Al content, as expected. The sheet resistances start to increase due to the irradiation with O\textsuperscript{+} ions at the fluence of 10\textsuperscript{13} cm\textsuperscript{-2}. Differences between the differently doped samples appear at fluences of about (3–4) × 10\textsuperscript{13} cm\textsuperscript{-2}. The R\textsubscript{S} of the undoped sample and the sample with [Al]=2 × 10\textsuperscript{18} cm\textsuperscript{-3} are similar at all fluences. R\textsubscript{S} increases rapidly up to 10\textsuperscript{14}–10\textsuperscript{15} Ω/sq at the fluence of 10\textsuperscript{14} cm\textsuperscript{-2}. The behavior of the sample with [Al]=5 × 10\textsuperscript{18} cm\textsuperscript{-3} becomes different at the fluence of 6 × 10\textsuperscript{13} cm\textsuperscript{-2}. It increases slower with fluence until 10\textsuperscript{15} cm\textsuperscript{-2}, at which the sheet resistance saturates at a lower value of 2 × 10\textsuperscript{10} Ω/sq. In the heaviest doped sample, the sheet resistance increases much less than in the other samples. It saturates at a fluence of 3 × 10\textsuperscript{13} cm\textsuperscript{-2} at a value of 1.2 × 10\textsuperscript{4} Ω/sq, indicating that when doped with Al higher than 5 × 10\textsuperscript{18} cm\textsuperscript{-3}, ZnO cannot become isolated even at fluences as high as 10\textsuperscript{17} cm\textsuperscript{-2}.

The sheet resistance measurements presented above can be explained in the light of the positron experiments. Prior to irradiation, the density of carriers (electrons) is 5
$10^{17}$ cm$^{-3}$ in the undoped sample and equal to the Al content in the doped samples. The maximum Zn vacancy concentration after irradiation before the formation of vacancy clusters is around $(2-5) \times 10^{18}$ cm$^{-3}$, the same in undoped and doped samples. Here it is worth noting that this value is similar to the carrier concentration of the sample with [Al] = $5 \times 10^{18}$ cm$^{-3}$ which gets partially isolated.

In the undoped sample, the sheet resistance saturates when the Zn vacancy concentration is $2 \times 10^{17}$ cm$^{-3}$, a value comparable to the initial carrier concentration. The maximum electrical isolation due to the compensation of Zn vacancies occurs after irradiating to a fluence of $10^{15}$ cm$^{-2}$. At higher irradiation fluences, newly created vacancy clusters do not increase the electrical isolation level of the samples, indicating that the vacancy clusters are electrically inactive. Thus, the samples that become isolated (initial carrier concentration below $10^{19}$ cm$^{-3}$) are isolated by the introduction of compensating Zn vacancies as proposed previously by Kucheyev et al. Possibly a similar concentration of negatively charged nonopen volume defects are also introduced as they have been measured in electron-irradiated and as-grown samples.

It should be noted that the sample with the highest doping level shows a different behavior from the rest. $R_s$ saturates at $3 \times 10^{13}$ cm$^{-2}$ and its value is 8 orders of magnitude lower than in the undoped sample. This is consistent with the Zn vacancy concentration having an upper limit in the range of $(2-5) \times 10^{18}$ cm$^{-3}$ in the irradiated samples, i.e., that above this concentration all the excess Zn vacancies are bound to electrically inactive vacancy clusters. Hence the Zn vacancy concentration in the highest doped samples never reaches a level that could fully compensate the Al donors, and the resistivity increases only moderately compared to the lower doped samples. The small increase at low irradiation fluences, below mid-$10^{13}$ cm$^{-2}$, where no or very little changes are observed in the positron data, is likely related to the combined effect of reduction of mobility and the production of compensating centers. We have shown that the compensation comes from the introduction of acceptor centers: Zn vacancies and possibly negatively charged nonopen volume defects. The reduction of mobility could be related to the scattering with newly introduced defects that include some other defects as oxygen vacancies or other donor-type defects.

### CONCLUSION

We have studied the electrical isolation of thin ZnO layers irradiated with 2 MeV O$^+$ ions to various fluences by combining sheet resistance measurements and positron annihilation spectroscopy. Our results indicate that Zn vacancies, the dominant defects detected by positrons, are produced in the irradiation at a relatively low rate of about 2000 cm$^{-1}$ when the ion fluence is at most $10^{15}$ cm$^{-2}$ and that vacancy clusters are created at higher fluences. The Zn vacancies introduced during the irradiation process act as dominant compensating centers and cause the electrical isolation in samples with Al doping of at most $5 \times 10^{18}$ cm$^{-3}$, while the results suggest that the vacancy clusters are electrically inactive. The high mobility of Zn sublattice defects (zinc vacancies or interstitials) is the likely cause for both the low introduction rate and fast clusterization of the Zn vacancies.

### ACKNOWLEDGMENTS

This work was partially supported by the Academy of Finland. We would like to thank I. Makkonen and M. J. Puska for providing the calculations of the Doppler curves.

---

8 asier.zubiaga@tkk.fi