ELECTRONIC BARRIERS PRODUCED AT ZnO SURFACES BY ION IMPLANTATION AND ANNEALING

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ABSTRACT

Modern varistors are made of polycrystalline ZnO, doped to create Schottky-like barriers at the grain boundaries. To allow the study of tailored single barrier junctions, we have implanted ZnO crystals with Bi, Sb and transition metals. The electrical properties and the distribution of Bi and Sb were measured in the implanted crystals as a function of annealing temperature. After implantation and before heating, no barriers can be observed. After heating to 600-800°C, a high voltage (insulating) barrier is created. Heating to above 1000°C produces a 2-1/2 Volt barrier with high nonlinearity. The temperatures at which these barriers appear correspond, respectively, to temperatures at which motion of Sb and Bi first can be observed by ion backscattering techniques, and at which these elements diffuse freely.

INTRODUCTION

Most modern varistors are made of polycrystalline ZnO, doped to create Schottky-like barriers at the grain boundaries [1]. There is widespread agreement that these barriers are due to electron depletion of a subsurface region of the ZnO grains [2]. However the relationship between the barriers and the dopants used to produce them is not clearly understood. To allow the study of tailored simple barrier junctions, ZnO crystals have been implanted with Bi, Sb, and transition elements. In this paper we report on the electrical properties and on the dopant distributions of these samples as implanted and as heated to temperatures up to 1200°C.

EXPERIMENT

ZnO plates, approximately 4x4x0.8 mm were cut, approximately perpendicular to the hexagonal axis, from larger single crystals purchased from Airtron [3]. The purchased crystals were on the whole clear and transparent, with some parts tinted green. Analysis of clear portions of the samples indicated the presence of the following impurities: Ba, 10 μg/g; Fe, Si, Al, 5 μg/g; K, Na, Mg, 1 μg/g. Tinted regions were discarded. One of the two large surfaces of each plate was polished with SiC paper of progressively finer grit, with the final polish being done with a vibratory polisher using 0.3 μm Al_2O_3.

The polished surfaces were implanted, either with Bi, or with Bi, Sb, Cr, Co, and Mn. A 200-KeV Varian ion implanter was used and the accelerating voltages were adjusted so that the maximum concentrations of all the dopants in a given sample came to rest at the same depth. Table I indicates the accelerating voltages used, the depths of implantation, and the number of ions implanted.

Two sets of samples were annealed. One set was used only for measurements of the current/voltage characteristics. These samples were used in pairs; sandwiches were made from two plates with the implanted surfaces in

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Table I. Depth and Number of Implanted Ions

Sample Set	Ion	Energy (keV)	Depth (A)	Number Implanted (Ions/cm^2)
1	Bi^{++}	120	388	2×10^{15}
	Sb^{+}	175	387	4×10^{15}
	Cr^{+}	90	380	2×10^{15}
	Mn^{+}	95	386	1×10^{15}
	Co^{+}	105	396	1×10^{15}
2	Bi^{++}	120	388	1×10^{16}
3	Xe	150	331	2×10^{16}

contact throughout the anneals and electrical measurements. A furnace insert made of alumina and Pt contact wire was used to hold the samples together. This insert could be moved to the electrical measuring equipment without disturbing the samples. A second set of samples which was used primarily for Rutherford backscattering experiments was annealed in an MgO crucible. Temporary sandwiches of these samples were made for electrical measurements after each anneal.

The anneals were performed in air. The samples were heated to the annealing temperature in 2-4 hours, held at the anneal temperature for 15 min, and cooled in the furnace with a maximum cooling rate of 7°C/min.

Ion backscattering measurements of the dopant depth distributions were made using 2 MeV ^{4}He ions. Scattered particles were detected and energy analyzed by a silicon surface barrier detector at a scattering angle of 150° giving a depth resolution of ~10 nm. The beam diameter was approximately 1 mm.

Voltage vs current measurements were performed using dc excitation at increasing voltages of one polarity, followed by a similar set with reversed polarity. For the cases when the current decreased after a given voltage was applied, (usually when an electronic barrier was present) equilibration was allowed before data recording until either the current stabilized or 10 min had passed. Electrodes were normally Pt, 2 to 3 mm in diameter, sputtered on the back (unimplanted) surfaces of the ZnO samples. In a few cases Ag paint electrodes were painted on for electrical measurements and removed with acetone immediately thereafter. Results were not dependent on electrode type.

RESULTS

A. Electrical Properties

Typical behavior upon heating ZnO sandwich samples, implanted respectively with Bi or the 5 dopants indicated *in Table I is depicted in Figs.* 1 and 2. Before annealing the samples exhibit approximately ohmic behavior (current, I, proportional to voltage, V) with resistances between 10^3 and 10^5 ohms. Heating to 200°C causes little change. As anneals are performed

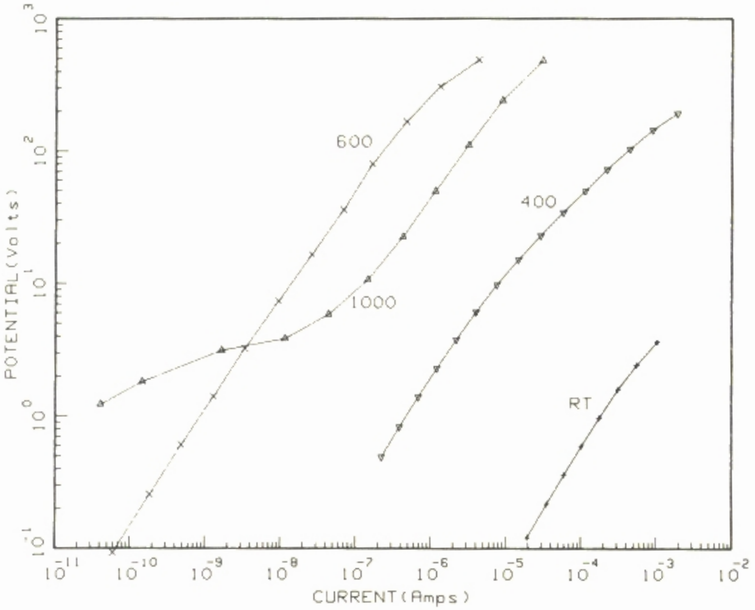

Fig. 1: Electrical characteristics of a Bi implanted ZnO crystal sandwich annealed at increasing temperatures. The labels indicate anneal temperatures in °C.

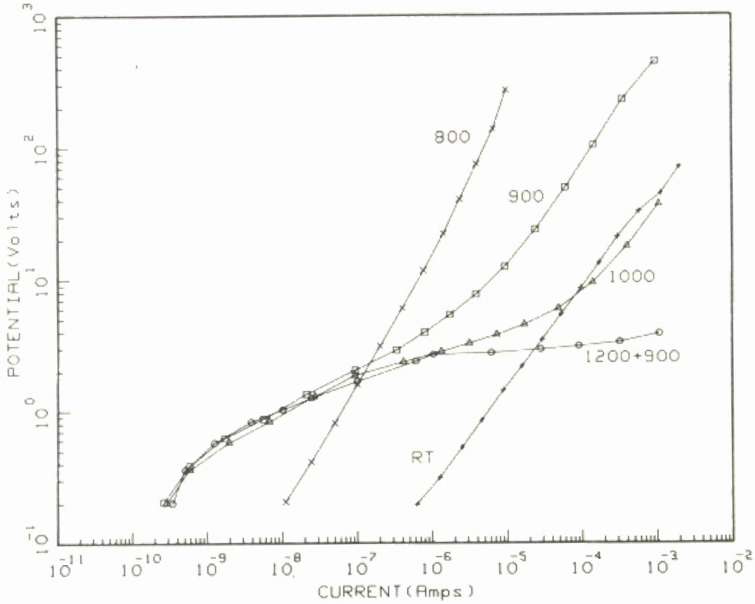

Fig. 2: Electrical characteristics of two ZnO crystals implanted with Bi, Sb, Mn, Co, and Cr, with the implanted faces in contact. The curve labels indicate anneal temperatures in °C.

at increasing temperature up to approximately 800°C, resistance of the sandwiches increases to near 10^9 ohms. These barriers can be degraded (so that their resistance decreases) when currents greater than 10^{-4} A are sent through them; however it is of interest that after 800°C annealing, when the barriers have high resistances, voltages as high as 200 V do not destroy them.

Further heating to 1000-1200°C is necessary to establish the nonlinearity normally associated with varistor barriers. As indicated for the 5-element implanted sample, heating to 1200°C and furnace cooling produces low resistance sandwiches; however subsequent reannealing at 900°C for 15 minutes produces relatively high nonlinearity with breakdown voltages of 2 to 3 volts [4]. Repeated cycling to 1200°C and 900°C in two different sandwich samples reproduced, respectively, the ohmic behavior or the nonlinear, 2-3 volt barrier.

For comparison two ZnO samples were implanted with xenon, presumably a chemically inert element. They were formed into a sandwich and heated in the same fashion as the samples described in the previous paragraph. The high voltage barrier between 600 and 800°C was observed in these samples as well (5×10^9 ohms after 700°C), but no nonlinearity appeared at higher temperatures. Instead the resistance decreased to below the room-temperature value.

The samples annealed in crucibles (not held together by spring tension) also exhibited the high voltage barriers for anneals below 800°C. They did not show reproducible 2-3 volt barriers. Instead there appeared increasing nonlinear voltage-current behavior after anneals at 1000°C or at 1200°C followed by 900°C. However, the voltage in the nonlinear region was nearer 10V, indicating the presence of multiple barriers. Moreover, the tendency of these sandwiches to be degraded by currents above 10^{-4} amps was greater than for the samples annealed and measured in the sample holder where they remained in contact.

B. Ion Backscattering Measurements

Of the five elements implanted in ZnO only the heavy elements, Bi and Sb can be easily observed by backscattering. Figures 3 and 4 show portions of the ion back scattering spectra that include the zinc edge and peaks corresponding to Bi and Sb implanted layers. Figure 3 is for a 5-element implanted surface; Fig. 4 is for a Bi implanted one. The different spectra were obtained after successive anneals at the temperatures indicated. For the samples implanted with 5 elements (see Fig. 3) no change in Bi or Sb distribution was observed below 800°C. Between 800°C and 1000°C, however, the Sb distribution flattened and almost all of the Bi disappeared. After the samples had been heated to 1200°C only a very small amount of Bi remained; it seemed to be distributed uniformly and not primarily at the surface. For samples implanted with 10^{16} Bi ions (see Fig. 4) we observed a slight narrowing of the distribution and an increased asymmetry (compare squares and circles in Fig. 4) after heating to 600 and 800°C. At 1000°C most of the Bi in the bulk of the ZnO had disappeared and a small amount remained at or close to the surface. After annealing at 1200°C only a tiny residue of the implanted Bi remained; it appeared to be distributed uniformly and not concentrated at the surface. Additional annealing at 900°C did not give rise to any observable changes in the ion backscattering spectra.

The data of Figs. 3 and 4 are typical of the behavior of a number of identically treated samples. However, small differences were observed for different samples in the amount and the depth distribution of bismuth and

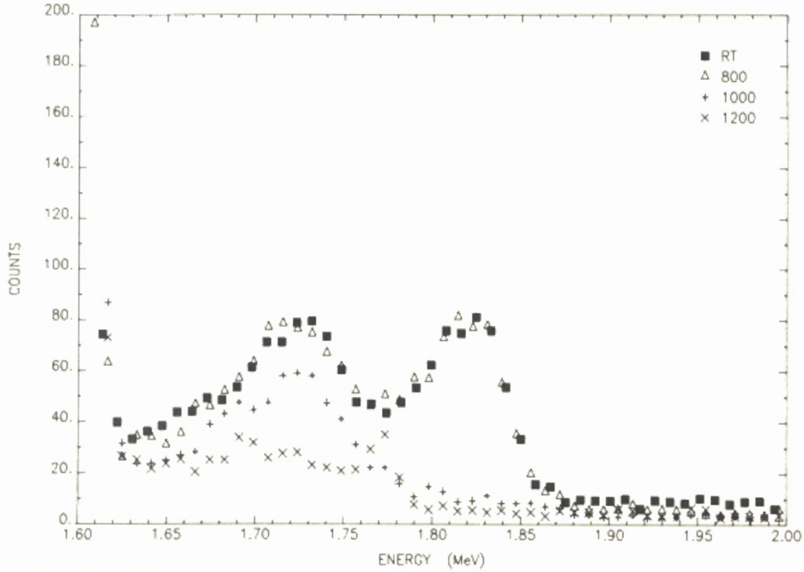

Fig. 3: ^{4}He backscattering spectrum for ZnO implanted with Bi, Sb, Mn, Cr, and Co, annealed at increasing temperatures. ■, before heating; △, 800°C; +, 1000°C; x, 1200°C followed by 900°C.

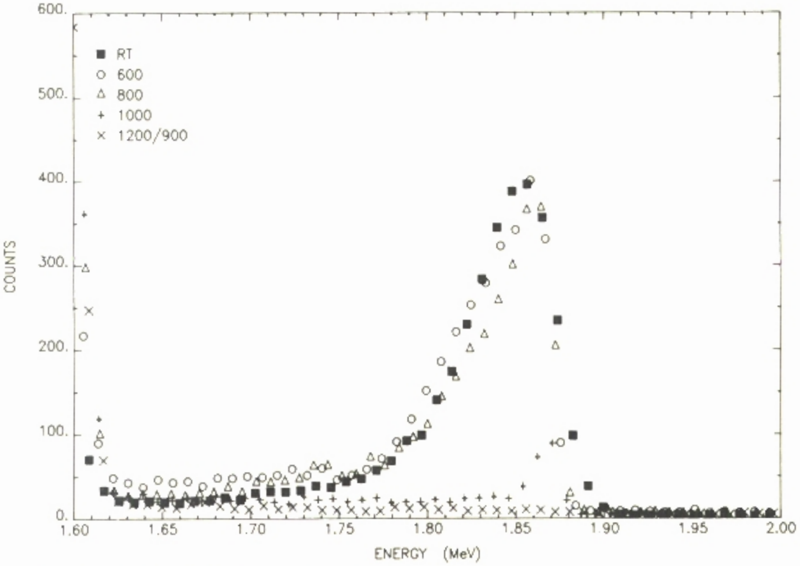

Fig. 4: ^{4}He backscattering spectrum for a Bi implanted ZnO crystal annealed at increasing temperatures. ■, before heating; ○, 600°C; △, 800°C; +, 1000°C; x, 1200°C followed by 900°C.

antimony after 800°C and 1000°C annealing. An ion backscattering spectrum obtained on a piece from one of the permanent sandwiches that had been used for electrical measurements and had been annealed up to 1200°C looked identical to the corresponding spectrum in Fig. 3.

DISCUSSION

It is significant that implantation without heating produced no stable barriers. Annealing at temperatures between 600 and 800°C produced insulating barriers and heating to at least 1000°C (the best treatment consisted of a 1200°C anneal followed by one at 900°C) was required to produce nonlinear behavior attributable to a single varistor barrier. The temperature ranges necessary to produce these two types of barriers correspond to temperatures where, respectively, the implanted impurities just begin to move, and where they move freely.

The fact that the bismuth, as implanted, does not give rise to a barrier indicates that the presence of this element in the bulk of ZnO is not sufficient; a surface (or grain boundary) is necessary, and presumably trivalent Bi either acts to adjust the oxygen/zinc ratio [5] at the surface or produces surface electron traps. Our ion scattering results show clearly that no thick Bi layer is necessary to produce varistor action. This is in accord with observations of actual varistor grain boundaries [6] where no Bi rich phase separated the ZnO grains.

The high voltage barriers we observed after 600-800°C annealing were unexpected. We propose two possible explanations. One is that the implanted impurities or the radiation produced defects [7] readjust during the 600-800°C anneal to form centers that give rise to deep electronic traps. Such electron trapping would produce a thick enough insulating layer to stand up under voltages up to 500V. The other possibility is that multiple small angle grain boundaries exist in the surface region of the ZnO crystals. These could be due to the presence of boundaries in the original crystal, or due to creation of them during sample preparation (slicing and polishing) or implantation. Annealing at 1200°C is known to allow recrystallization. Laue x-ray photographs indicating multiple Laue spots in at least one of our unannealed samples support the second explanation. Further work with better crystals and more carefully characterized surfaces should allow us to account for the high voltage barriers.

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