Laser fabrication of electrodes on zinc oxide varistors

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Near surface properties are reported for ZnO varistors irradiated with high-intensity pulses from both KrF excimer and CO_2 lasers. Electrical, optical, and Rutherford backscattering measurements reveal that a thin conducting film is formed by pulsed-laser heating of a varistor surface. The conductive film is evaluated as a varistor electrode.

INTRODUCTION

In the course of examining effects of laser radiation on ceramics, it was discovered that a zinc oxide surface acquires a metallic luster and an increased electrical conductivity following irradiation by a pulsed laser. This discovery prompted an investigation, which is reported here, both of the nature of the laser-induced surface changes and of the feasibility of fabricating electrodes on ZnO varistors by using lasers. The investigation focused almost exclusively on varistors because they undergo laser-induced changes that are similar to, but of more interest than, those of pure ZnO. Varistors are sintered ceramic aggregates of ZnO grains with a few percent of impurities such as Bi, Sb, and Co, which are deliberately added.[1] Varistors have unusual electronic properties that derive from Schottky-type grain-boundary barriers, and their extremely nonlinear electrical resistance is used in voltage-clamping and surge-arrester applications. Electrodes are an integral part of a varistor and of its manufacture. Although a varistor's electrodes have little influence on its electrical characteristics, they may influence varistor stability or initiate failures.

There is general interest in the effects of high-intensity laser pulses on materials, and there have been few studies of the effects of lasers on widegap binary semiconductors such as ZnO. Zinc oxide has a 3.2-eV band gap and a strong reststrahlen absorption near 10 μm. Thus, either ultraviolet or infrared lasers couple efficiently to ZnO, although in fundamentally different ways. Ultraviolet radiation couples to the electronic system of ZnO and is converted to heat by the electron-lattice interaction. In contrast, infrared light generates heat by coupling directly to the lattice. It is interesting to compare the effects of ultraviolet lasers to those of infrared lasers, and both a KrF excimer laser with a wavelength of 248 nm and a CO_2 laser with a wavelength of about 10.6 μm were used in the investigation.

RESULTS

Electrodes were made on commercial varistor ceramics (General Electric V130LA10A) using high-intensity, submicrosecond pulses from both a KrF excimer laser and a CO_2 gas laser. The electrical characteristics of a varistor with electrodes fabricated using an excimer laser are compared in Fig. 1 to those of a varistor with electrodes made of a silver paint; the dc electrical characteristics show typical varistor nonlinearities and are virtually identical. Photographs of the two varistors are inset on Fig. 1. The laser creates a coating with a metallic luster that is quite visible. More highly conductive coatings were obtained with the excimer laser than with the CO_2 laser, probably because the excimer laser light is more strongly absorbed than the CO_2 laser beam. Energies of a few tenths of a J/cm^2 per pulse from the excimer laser will form an electrode, whereas a few J/cm^2 per pulse required from the CO_2 laser.

Information on the thickness and composition of the electrodes was obtained from Rutherford backscattering (RBS) measurements (scattering yield versus energy) made before and after laser irradiation of a varistor surface. Figure 2 shows RBS spectra from 2-MeV ^{4}He ions incident along the surface normal and detected at a backward scattering angle of 150°. In RBS spectra, the energy scale reflects two variables: (1) the atomic mass of scattering ions, and (2) the depth of the scattering ions below the surface. The heavier the scattering ion, the higher will be the energy of the scattered He ion; the deeper the scattering ion is within the sample, the more energy will be lost by the He ion in traversing the sample and the lower the energy of the detected He will be. Accordingly, the edges of the scattering yield at high energies correspond to the energies of backscattering by heavy atoms (Bi,Sb) at the surface.

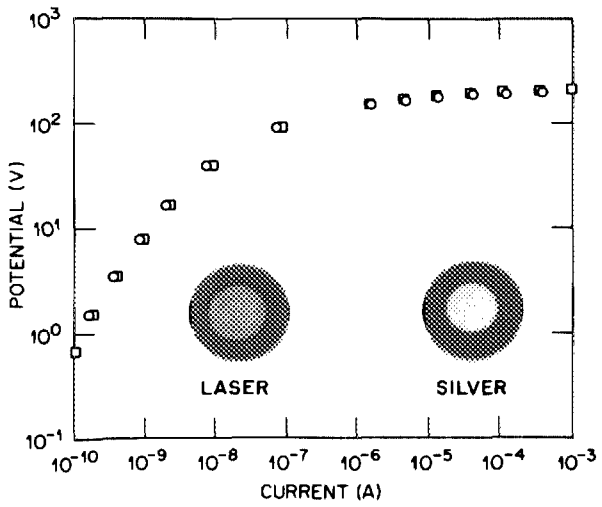

FIG. 1. A comparison of the electrical characteristics of varistors having electrodes fabricated using a KrF excimer laser and made with silver paint. The inset shows photographs of the varistors; the varistor with laser-fabricated electrodes is on the left.

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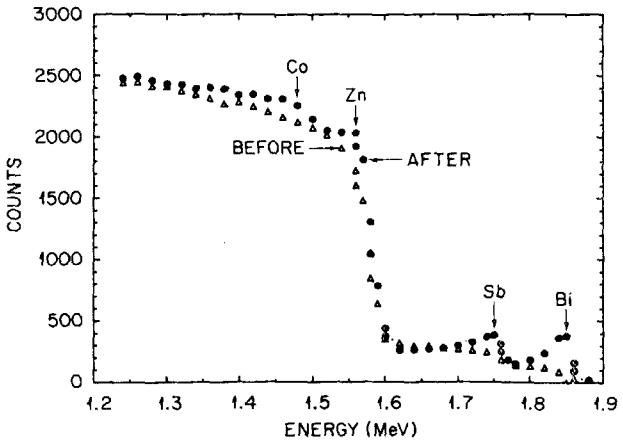

FIG. 2. Rutherford-backscattering measurements made before and after a varistor was irradiated with an excimer laser. The results were obtained for 2-MeV alpha particles backscattered at an angle of 150°. The beam current was 10 nA for a total integrated charge of 60 μC.

The effects of laser irradiation on ZnO varistors are manifested in the RBS spectra by the appearance of peaks corresponding to the energy of scattering from Bi, Sb, Zn, and Co at the surface. The peaks are attributed to the increase of the surface concentration of these elements due to the laser heating. The depth distribution of Bi and Sb in the near-surface region can be derived from the widths of the peaks. It is estimated that the excess metal ions are present to a depth of about 0.1 μm. Beyond that depth, the laser-treated surface has the same composition as the untreated varistor, as indicated by the fact that the two curves coincide for energies 0.07 MeV or more below the Bi or Sb edges.

Optical measurements confirm that the laser irradiation does not produce a thick metallic coating. Infrared reflectance spectra of a varistor measured before and after irradiation by an excimer laser are compared in Fig. 3 to each other and to a spectrum of polished zinc metal. The nearly constant, high infrared reflectance of the zinc is typical of a highly conductive metal.[2] The varistor spectra exhibit peaks

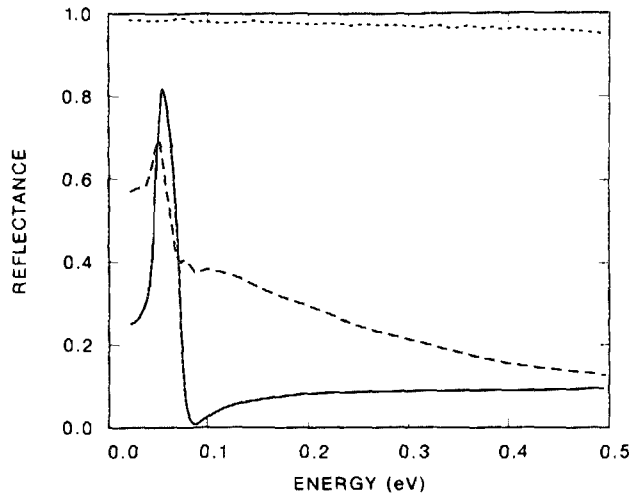

FIG. 3. Infrared reflectance spectra of a ZnO varistor measured before (solid curve) and after (dashed curve) treatment with an excimer laser. The reflectance of zinc metal is also shown (shorter dashes).

near 0.05 eV that are associated with the ZnO reststrahlen absorption. The position of the infrared reflectance minimum, which is seen near 0.1 eV in the spectrum of the unirradiated varistor, is a function of the carrier concentration and can be used to gauge the grain resistivity and carrier concentration of ZnO varistors.[3] A resistivity of 0.3 Ω cm and a carrier concentration of $3\times10^{17}/\text{cm}^3$ are deduced from the spectrum. When the varistor surface is laser irradiated, the reflectance minimum vanishes, and the reflectance increases by almost two orders of magnitude at the energy of the minimum. The reststrahlen peak does not disappear. Thus, a substantial change in the electrical conductivity is revealed, but the reflectance of the irradiated surface is not that of a thick, uniform coating of a good metal.

The van de Pauw technique[4] was used to measure the electrical properties of laser-fabricated electrodes. Because the varistor ceramic only conducts significantly at relatively high voltages, at low voltages the electrode properties can be measured independent of the underlying ceramic. The sheet resistivity of the electrodes was measured to be about $10^3\ \Omega$; from Hall voltage measurements a sheet carrier concentration of approximately $2\times10^{15}/\text{cm}^2$ and a Hall mobility of about 3 $\text{cm}^2/\text{V sec}$ were deduced. If a uniform surface layer is assumed and the thickness calculated from the backscattering data is used, a bulk resistivity of about $10^{-2}\ \Omega$ cm and an electron concentration of about $10^{20}/\text{cm}^3$ is computed. These values can be compared with the ZnO grain resistivity and electron concentration of 0.3 Ω cm and $3\times10^{17}/\text{cm}^3$, respectively, that are obtained from the infrared reflectance spectrum of the varistor before laser irradiation. Thus, the electrode has a relatively large carrier concentration, but the carriers have low mobility. The electrode resistance has a negative temperature coefficient; the resistivity increases by about a factor of 2 between room temperature and liquid-nitrogen temperature. It can be concluded from the magnitude and temperature coefficient of the resistivity that the electrode is a semiconductive coating rather than a metallic film.

The current-carrying capability of the laser-fabricated electrodes was investigated. Because the electrodes are thin and are not excellent conductors, the electrodes may fail before the varistor ceramic if the electrical contacts to the electrodes are too small. In tests employing high current pulses (e.g., 10 A/cm^2 for 1 ms) through the varistor, the electrodes failed when the contact area was less than about $10^{-2}\ \text{cm}^2$. Both these tests and rough calculations indicate that the maximum current density in the electrodes should be limited to about $10^4\ \text{A/cm}^2$ for millisecond pulses. Even though varistors are typically designed for a maximum current density in the ceramic of only about 10 A/cm^2 in a 1-ms pulse, the lateral currents in the electrodes will exceed $10^4\ \text{A/cm}^2$ if the contacts to the electrodes are very small.

DISCUSSION

Because the surface produced on ZnO by high-intensity laser pulses has a metallic luster, it was originally supposed that a film of zinc metal was formed. However, the electrical, optical, and backscattering results reveal a semiconducting thin film that is primarily comprised of ZnO. The film differs

from the underlying ceramic because of its higher carrier concentration and lack of grain-boundary barriers. Nevertheless, all the properties of the coating are found within ranges known for heavily doped ZnO. The low Hall mobility is readily attributed to strains caused by the heating and cooling, grain boundaries, or defects, but it is not atypical of ZnO thin films in any case.[5] Moreover, it is possible that the electronic barriers in the surface layer are not completely and totally destroyed by the laser irradiation. The backscattering results suggest a gradual merging of the surface with the varistor ceramic rather than an abrupt interface.

In spite of the thinness and modest electrical conductivity of the surface film, it performs adequately as a varistor electrode. Moreover, because no effort was made to optimize electrode fabrication, it is probable that the process can be improved. In particular, it may be possible to improve the carrier mobility in the film, since much greater carrier mobilities (e.g., 120 cm^2/V sec) have been attained in thin ZnO films.[6] However, because the laser-fabricated electrodes replace inexpensive conductive paints or flame-sprayed metals, there is no obvious financial incentive for the laser process. Nevertheless, it is of interest as an example of laser processing methods; to mention one potential application, the process may be adaptable to the fabrication of thin films for use as gas sensors.[7]

The laser-induced changes in the surface of a ZnO varistor can be interpreted as a result of thermal heating. The energy in the submicrosecond, high-intensity laser pulses is sufficient to heat the varistor surface to above the ZnO sublimation temperature of 1700 °C. The electrically conductive coating forms on the varistor surface because oxygen, being the most volatile of the varistor constituents, is lost more readily from the heated surface than is zinc or the dopant metals. The surface is modified more readily by an excimer laser than by a CO_2 laser because the absorption coefficient for 248-nm light is about 10^5 cm^{-1}, but the absorption coefficient is only about 10^2 cm^{-1} for 10.6-μm light.[5] Thus, the energy of the CO_2 laser is deposited over a greater depth, and more energy is required to heat the surface to the sublimation temperature.

Nakayama and Itoh also investigated the effects of pulsed-laser radiation on ZnO.[8,9] These researchers used a mass spectrograph and time-of-flight measurements to examine the particles emitted from a ZnO surface heated with a pulsed nitrogen laser (photon energy = 3.68 eV). They found that Zn, O, and O_2 are emitted in nearly equal numbers for laser intensities above a threshold value of 0.16 J/cm^2, findings that are in accord with our results. They also found that the energy distribution of the emitted particles deviates from a Maxwellian distribution. This they interpreted as evidence that particle emission results from a laser-generated electron-hole plasma at the ZnO surface, rather than from thermal effects.[10] However, after much controversy, models involving thermally induced rather than plasma-induced phase transitions on a submicrosecond time scale are now generally accepted.[11] Moreover, the successful use in our work of a CO_2 laser, which couples to the ZnO lattice rather than to the ZnO electronic system, clearly supports the thermal interpretation.

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