UV modification of zinc oxide

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Surface nanoparticles of zinc metal and bulk zinc and oxygen vacancies are produced by irradiation of single-crystal zinc oxide with 193nm excimer-laser light.

In its hexagonal, wurtzite form, crystalline zinc oxide (ZnO) is a semiconductor with a direct, wide bandgap of 3.3eV and a range of actual and potential applications. It is often used for laser and light-emitting diodes in the blue to UV and its healthy quantum efficiency makes it a strong candidate for energy-efficient lighting applications. In addition, ZnO can be used as a transparent conducting oxide coating and has potential for use in solar cells, LCDs, and flat-panel displays. When doped with manganese and cobalt, ZnO has possible applications in spintronics, a new technology that exploits the spin of electrons. However, a number of potential applications require robust p-type doping (which creates an abundance of positive-charge-carrying ‘holes’ in the semiconductor). This has yet to be achieved.^{1–3} As a result, there is intense interest in understanding ZnO.¹

In principle, zinc vacancies can serve as p-type acceptors. In many transparent, wide-bandgap materials such as ZnO, nanosecond UV-laser radiation creates excitations that decay to yield defects, such as chlorine vacancies in sodium chloride (table salt), easily seen by visible coloration of the crystal. Yet similar treatments with nanosecond pulses do not normally produce lattice defects in ZnO. Rather, any resulting defects are soon annihilated by the rapid diffusion of zinc and oxygen atoms back to their original lattice positions. This accounts for the very high resistance of ZnO to radiation damage.^{2,4}

However, using a bigger hammer—6.3eV photons from an argon fluoride excimer laser—we have generated gray to black spots on ZnO⁵ (see Figure 1). If this were a new type of color center, it would have to be called the ‘smudge’ defect. We used a variety of spectroscopic methods for further investigation and found that irradiation produces metallic zinc nanoparticles on the surface as well as zinc and oxygen vacancies in the bulk.

We found that UV-visible absorption spectra of the surface material are remarkably similar to that of metal zinc films. Both x-ray and Auger photoelectron spectra indicate the presence of metallic zinc and selected-area x-ray

Figure 1. Single crystal of zinc oxide showing three spots (1–3) irradiated with increasing pulsed-UV laser intensity (at a wavelength of 193nm): (1) 200, (2) 350, and (3) 500mJ/cm².

diffraction showed peaks due to crystalline zinc metal. We used time-resolved quadrupole mass spectroscopy to identify intense emissions of atomic and molecular oxygen, O and O₂, during irradiation in vacuum. Weaker emissions of atomic zinc were observed, consistent with metallic zinc being left behind. Most intriguingly, this surface zinc takes the form of nanoparticles, typically 10–20nm in diameter (see Figure 2). Careful transmission-electron-microscopy studies indicate that this zinc is confined strictly to the irradiated surface and, therefore, that the underlying bulk is free of nanoparticles. Metallic nanoparticles display interesting electronic and optical properties and usual production methods are complex compared to this example. Positron-annihilation spectroscopy of irradiated ZnO showed signals from the near-surface bulk due to zinc vacancies. Surfaces exposed at slightly higher laser-power densities in our laboratory provided tantalizing

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Figure 2. Scanning-electron-microscope images of a region within the laser-darkened area. (a) High density, higher laser fluence, (b) lower density, lower laser fluence. Electron diffraction shows that these nanoparticles are composed of metallic zinc.

evidence for p-type conductivity following chemical removal of any surface zinc.

We believe that hot electron-hole pairs generated by the laser (within an absorption depth of $\sim 200\text{nm}$) are responsible for the production of interstitials and vacancies. We are currently studying the details of the emission mechanisms. Interstitial O and Zn are both highly mobile.⁴ Interstitial oxygen that reaches the surface can be emitted, while interstitial zinc surface aggregates to form the observed nanoparticles. Note that all of these experiments are carried out in vacuum ($<10^{-7}\text{Pa}$). If laser irradiation is carried out in air (which contains oxygen) no darkening is observed, presumably because of complete oxidation of the Zn as it emerges on the surface. Vacuum-darkened crystals exposed to air (see Figure 1) remain dark because the zinc nanoparticles form a passivating oxide layer, preserving the metallic core.

In summary, this graying process is remarkable for a ‘radiation-hard’ material that is generally considered impervious to UV radiation. Ongoing work aims to understand the effects of laser radiation on ZnO, e.g., to know whether oxygen holes are produced as well as zinc vacancies. We are planning further studies on more efficient nanoparticle formation and doping and the effects of sample preparation and treatment. We also wish to investigate the plasmonic properties of the nanoparticles, nanostructures⁶ of ZnO, and the interface between the two, all of which may have important applications in electronic and photonic devices.

This work is done in collaboration with Lynn Boatner of Oak Ridge National Laboratory, who specializes in growth of single crystals, and Wayne Hess of Pacific Northwest National Laboratory, an expert in laser interactions with wide-bandgap materials.

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Enamul Khan is a PhD student. His work focuses on understanding the mechanisms of ionic, neutral atom, and molecular emissions from wide-bandgap materials induced by laser irradiation.

Steve Langford is a senior research associate focusing on probing mechanisms of laser/materials interactions, including defect production and both surface and bulk modification of transparent materials.

Tom Dickinson is the Paul A. Anderson professor, eminent professor and Regents professor of physics. His laboratory conducts research in the fundamental processes leading to modification, etching, and analysis of wide-bandgap materials with applications in areas such as photonics, sensors, and nanotechnology. Dickinson is a Fellow of SPIE, the Materials Research Society, the American Physical Society, the American Vacuum Society, and the American Association for the Advancement of Science.

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