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Application of Ion Implantation for Synthesis of Copper Nanoparticles in a Zinc Oxide Matrix for Obtaining New Nonlinear Optical Materials

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Abstract—We have obtained a layered composite material by implantation of single crystal zinc oxide (ZnO) substrates with 160-keV Cu^+ ions to a dose of 10^{16} or 10^{17} cm^{-2}. The composite was studied by linear optical absorption spectroscopy; the nonlinear optical characteristics were determined by means of *Z*-scanning at a laser radiation wavelength of 532 nm. The appearance of the optical plasmon resonance bands in the spectra indicated that ion implantation to the higher dose provides for the formation of copper nanoparticles in a subsurface layer of ZnO. The new nonlinear optical material comprising metal nanoparticles in a ZnO matrix exhibits the phenomenon of self-defocusing and possesses a high nonlinear absorption coefficient ($\beta = 2.07 \times 10^{-3}$ cm/W). © *2004 MAIK "Nauka/Interperiodica".*

In recent years, much effort has been devoted to the research and development of new composites based on wide-bandgap semiconductors and insulators containing metal nanoparticles, which are promising materials for optoelectronics and nonlinear optics. The phenomenon of collective excitation of conduction electrons in such nanoparticles under the action of electromagnetic (light) waves, called the surface plasmon resonance, accounts for a selective optical absorption and gives rise to nonlinear optical effects in the same spectral range [1, 2]. As is known [3], materials with a high concentration of metal nanoparticles synthesized, for example, by ion implantation, possess pronounced nonlinear optical properties. For this reason, such composites can be successfully used in integrated optoelectronic devices, for example, in waveguides with nonlinear optical switching providing for signal conversion at short (pico- or femtosecond) laser pulse durations [3].

Previously, metal nanoparticles have been successfully synthesized in the matrix of zinc oxide (ZnO)—a wide-bandgap semiconductor characterized by an optical bandgap width of 3.8 eV (corresponding to 326.3 nm). The first study in this direction [4] was devoted to the synthesis of gold nanoparticles in a ZnO matrix. Presently available data on the synthesis of metal nanoparticles in ZnO [4–12], with indication of a particle size and the methods of synthesis (including ion implantation [5, 8]) and characterization, are summarized in the table. However, the ion implantation synthesis of cobalt nanoparticles described in [5] requires additional (postimplantation) thermal treatments, which complicates the technology of such composite materials. On the other hand, copper nanoparticles had been formed directly by low-energy ion implantation [8], but the particle size was so small that a postimplantation annealing was still required to enlarge them. It should be noted that there is a large number of other publications devoted to the implantation of various metal ions into ZnO, but the ion doses were so small that even subsequent high-temperature treatments did not lead to the formation of metal nanoparticles. For this reason, papers reporting on the ion doping of ZnO are not included in the table.

From the standpoint of effective manifestation of nonlinear optical properties, the most promising metals are those with a high density of free conduction electrons, in particular, copper [3]. This study was aimed at experimental verification of the possibility of obtaining a new nonlinear optical material directly by the synthesis of copper nanoparticles in a ZnO substrate by means of ion implantation, without any postimplantation treatments. As seen from literature indicated in the table, nonlinear optical properties of ZnO with dispersed metal nanoparticles have not been studied so far.

A composite material was obtained using single crystal ZnO substrates optically transparent in a broad spectral range (~500–1100 nm). This matrix was implanted with 160-keV Cu^+ ions at a dose of 1×10^{16} or 1×10^{17} cm^{-2} at a high ion beam current density (~20–50 $\mu A/cm^2$). The ion implantation was performed at room temperature in a vacuum of 10^{-6} Torr on an EATON 3204 implanter (Julich, Germany). The optical density spectra were measured using a Perkin-Elmer Lambda 19 spectrophotometer. The spectra of the absorption cross section were also modeled, within the framework of the classical theory of interaction between electromagnetic waves and a spherical particle (Mie's theory), using a method described elsewhere [13]. The nonlinear optical characteristics of samples were determined by the method of *Z*-scan using a setup described in [14] in which the material was probed by second-harmonic radiation of a Nd:YAG laser with a wavelength of 532 nm, a pulse duration of 55 ps, and a pulse energy of 0.2 mJ. In order to avoid thermal effects influencing the nonlinear optical characteristics, the laser pulse repetition rate was not increased above 2 Hz. The laser beam intensity was controlled within (1–5) × 10^8 W/cm^2, which excluded the optical breakdown of samples.

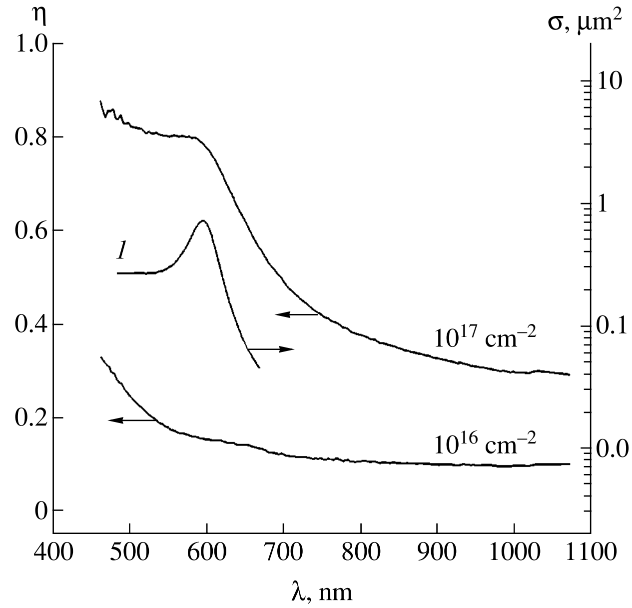

Fig. 1. Experimental spectra of the optical density η of ZnO implanted with copper to various doses, in comparison to the model spectrum of the absorption cross section σ calculated using the Mie theory (curve *1*) for a single 10-nm spherical particle in a ZnO matrix.

Figure 1 shows the experimental optical absorption spectra of the ZnO samples implanted with Cu^+ ions at different ion doses. For the sample implanted with copper to a lower dose, the spectrum is virtually identical to that of unirradiated ZnO, except for a somewhat increased absorption in a short-wavelength region

Metal nanoparticles in a ZnO matrix: types and methods of synthesis and diagnostics

Metal*	Method of synthesis	Method of diagnostics**	Particle size, nm	Authors
Co	Ion implantation and thermal annealing	XRD, SQUID	3.5	Norton *et al.*, 2003 [5]
Cu	RF sputtering and thermal annealing	OS, XRD, TEM	2–17	Varquer-Cuchillo *et al.*, 2001 [6] Pal *et al.*, 2004 [7]
Cu	Ion implantation and thermal annealing	OS	–	Kono *et al.*, 2003 [8]
Ru	Chemical deposition from solution	OS, XPS, SEM	2	Bozlee *et al.*, 2000 [9]
Pt	RF sputtering and thermal annealing	OS, XRD, TEM	1–15	Pal *et al.*, 2004 [7]
Au	Electrodeposition from solution	OS, TEM	5–50	Yoshino *et al.*, 1996 [4]
Au	Chemical deposition from solution	OS, XRD, SEM	5–40	Bozlee *et al.*, 2000 [9]
Au	Magnetron sputtering	OS, XRD, TEM	20–70	Liao *et al.*, 2003 [10]
Au	Laser ablation	OS, XRD, SEM	2–6	Tiwari *et al.*, 2003 [11]
Au	Sol-gel coating and thermal annealing	OS, XRD, SEM	50–100	Wang *et al.*, 2003 [12]
Au	RF sputtering and thermal annealing	OS, XRD, TEM	1–27	Pal *et al.*, 2004 [7]

* Metals are listed in order according to the Periodic Table; ** methods of diagnostics: OS, optical spectroscopy; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; SEM, scanning electron microscopy; TEM, transmission electron microscopy; SQUID, superconducting quantum interference device magnetometry.

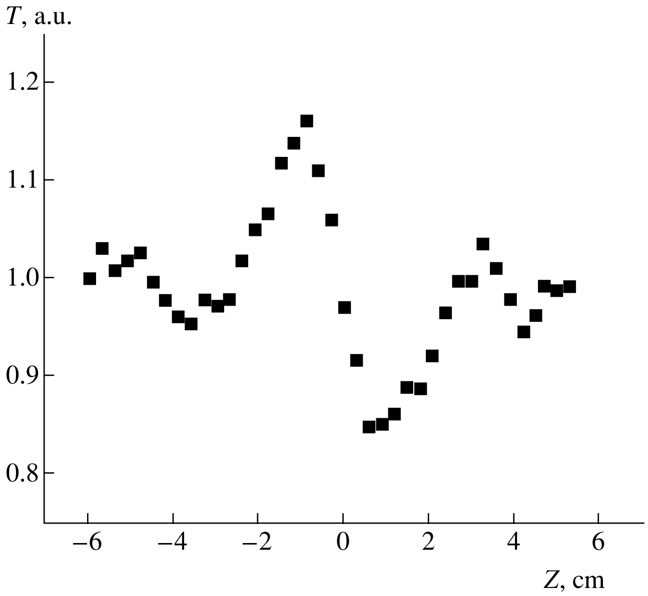

Fig. 2. Normalized transmission $T(Z)$ on the Z scale measured in the scheme with closed aperture for a ZnO matrix implanted with copper to a dose of 1×10^{17} cm^{-2}.

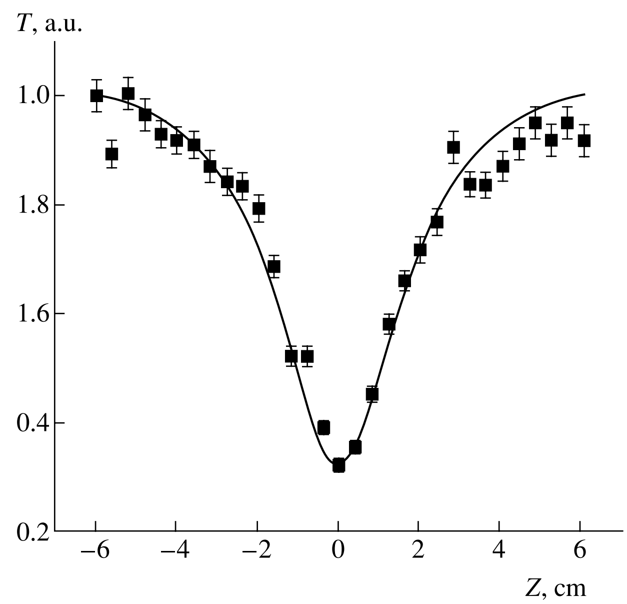

Fig. 3. Normalized transmission $T(Z)$ on the Z scale measured in the scheme with open aperture for a ZnO matrix implanted with copper to a dose of 1×10^{17} cm^{-2}. Solid curve shows the results of a model calculation.

(<450 nm), which is related to radiation-induced defects in the sample crystal. Therefore, we may conclude that this irradiation dose does not provide for the formation of sufficiently large (>2 nm) implanted copper particles capable of producing significant optical absorption due to the surface plasmon resonance. In contrast, a wide selective absorption band with a maximum at ~600 nm observed in the spectrum of the sample implanted at a higher dose is direct evidence of the formation of such copper nanoparticles exhibiting surface plasmon resonance [1]. For the comparison, Fig. 1 also shows a model spectrum of the absorption cross section calculated for a single 10-nm spherical particle in a ZnO medium, which is characterized by maximum optical absorption at the same wavelength. Thus, the calculation confirmed the possibility of formation of copper particles in a ZnO matrix. The difference between shapes of the model and experimental spectra is probably explained by the distribution of the synthesized metal nanoparticles with respect to size, which usually takes place during the ion implantation of dielectrics [2].

We believe that the main factor favoring the formation of larger nanoparticles of copper in ZnO, in the present case, in comparison to the results obtained in [8], is the higher ion beam current density used in our experiments. The surface energy density liberated in the course of stopping of the incident copper ions in our experiments was ~8 W/cm^2, which is more than 50 times the value reported in [8]. The high ion beam power ensures significant local heating in the irradiated ZnO layer, increases the diffusion mobility of implanted copper, and, hence, favors the effective nucleation and growth of metal nanoparticles.

The nonlinear optical characteristics were studied only using a ZnO sample implanted to a higher dose (1×10^{17} cm^{-2}), which was known to contain metal nanoparticles. Figures 2 and 3 show the results of measurements of the normalized transmission $T(Z)$ on the Z scale in the schemes with open and closed aperture, respectively. The shape of the $T(Z)$ curve in Fig. 2 shows that laser radiation is subject to nonlinear self-defocusing with a negative nonlinear refractive index. The complicated shape of this curve is probably determined by superposition of the effects of nonlinear refraction both from metal nanoparticles and from the ZnO matrix modified by the presence of these particles.

The character of the $T(Z)$ curve in Fig. 3 is evidence of a clear manifestation of the nonlinear optical absorption. For determining the nonlinear absorption coefficient β, we used an approach described in detail elsewhere [14]. The $T(Z)$ curve was modeled using a method proposed by Kwak *et al.* [15]. The obtained value, $\beta = 2.07 \times 10^{-3}$ cm/W, is significantly greater than that of the ZnO matrix (5×10^{-9} cm/W) for the same wavelength [16]. We believe that the high coefficient β of the composite is directly related to the presence of copper nanoparticles. It should be also noted that the value of β in our samples is two orders of magnitude higher than in a dielectric SiO_2 matrix with copper nanoparticles synthesized by ion implantation [17].

In summary, we have demonstrated the possibility of synthesizing large nanoparticles of copper in a subsurface layer of ZnO by ion implantation without subsequent thermal treatments. Using this method, we obtained a new nonlinear optical composite material, Cu:ZnO, exhibiting self-defocusing of laser radiation and possessing a high nonlinear absorption coefficient. The latter circumstance makes the new composite a promising material for active light intensity limiters in the visible spectral range.

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