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SCIENCE DIRECT
Surface & Coatings Technology 196 (2005) 30–33
SURFACE & COATINGS TECHNOLOGY
www.elsevier.com/locate/surfcoat

Nonlinear optical properties of Cu nanoparticles in various insulators fabricated by negative ion implantation

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Available online 27 September 2004

Abstract

Linear and nonlinear optical properties were studied for Cu nanoparticle composites with numerical calculation of the local electric field inside a nanoparticle. Negative Cu ions of 60 keV were implanted into amorphous SiO_2 and single crystals of $SrTiO_3$ and TiO_2 at a fixed dose rate of 10 $\mu A/cm^2$ to a total dose of 1×10^{17} ions/cm^2. The surface plasmon peak shifted to red and was enhanced with increasing refractive index values of the substrate. Complex nonlinear optical constants were evaluated by the z-scan method with a tunable femtosecond laser system over a range from 2.0 to 2.3 eV. The complex third-order optical susceptibility of the Cu:SiO_2 nanoparticle composite exhibited values of +1.6 to -3.1×10^{-9} esu around the surface plasmon resonance and took a maximum at 2.1 eV. The real part indicated negative values over the range and the imaginary part changed from positive to negative toward the higher photon energy. Both parts steeply vary with the photon energy near the surface plasmon resonance. The dispersion roughly reflects the local field factor.

Keywords: Photon absorption spectroscopy; Nanostructure; Metal nanoparticle; Ion implantation; Nonlinear optical susceptibility

1. Introduction

Metal nanoparticle composites, composed of isolated metal nanocrystals and insulating matrix, have large optical nonlinearities with picosecond response at the surface plasmon resonance [1–5]. The ultrafast response, ahead of electronic response in semiconductors, is of great interest for all-optical device applications. The enhanced nonlinearities recently attract much attention for application to the near-field optics, photonic device and photonic sensors because of interaction with an enhanced electric-magnetic field around a metal nanoparticle [6]. To design photonic devices, it is necessary to evaluate complex nonlinear constants of nanoparticles and the frequency dispersion. However, there have been very few experiment studies [7] of metal nanoparticle composites. For Cu nanoparticle composites, nonlinear optical constants at several wavelengths have been reported for the pulse duration of picoseconds [8–11]. The optical properties reflect the local electric field inside a metal nanoparticle. The local field depends on dielectric functions of metal nanoparticles and the matrix. Ion implantation is one of the most powerful techniques to fabricate metal nanoparticles in insulating substrates. Negative ion implantation has advantage of applicability to various ion species and insulating substrates, and has enabled us to form metal nanoparticles in various insulators and to design the demanded optical properties by selection of substrate and ion species [4,5].

In this paper, we present steady-state absorption and nonlinear optical constants of Cu nanoparticle composites, fabricated in insulators by negative ion implantation. We discuss enhancement of the surface plasmon resonance by the local field factor, the dispersion curve of complex third-order optical susceptibility, $\chi^{(3)}$ for pulse duration of 200 fs, of Cu nanoparticle composites, along with numerical calculations of the local field factor.

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0257-8972/$ - see front matter © 2004 Published by Elsevier B.V.
doi:10.1016/j.surfcoat.2004.08.083

2. Experimental

Negative Cu ions of 60 keV were produced by a Cs-assisted plasma-sputter-type ion source with a cusp magnetic field. The details of the techniques have already been described elsewhere [12]. A dose rate was fixed at 10 μA/cm^2, achieving a total dose of 1×10^{17} ions/cm^2. Insulating substrates used were amorphous (a-)SiO_2 and single crystals of $SrTiO_3$ and TiO_2. Implanted samples were annealed at 800 °C for a-SiO_2, and at 300 °C for $SrTiO_3$ and TiO_2, for 1 h in an Ar gas flow after the ion implantation. Depth distributions of Cu implants were measured by Rutherford backscattering spectrometry with 2.0 MeV He^+ ions and were analyzed using the RUMP program [13]. The Cu distribution of implanted a-SiO_2 was centered at a depth of 40 nm and the mean atomic fraction of Cu equal to 0.30 within a layer thickness of 20 nm.

The linear refractive index, n_0, of the substrates was determined by spectroscopic ellipsometry and yielded n=1.50 at 600 nm for a-SiO_2, 2.25 for $SrTiO_3$, and 2.58 for TiO_2. Steady-state absorption spectra were measured using a dual beam spectrometer. Measurements of nonlinear optical constants were carried out by means of the z-scan method [14] with a tunable femtosecond-laser system providing pulses of about 200 fs at 1 kHz. The pulse duration and repetition rate are possible to avoid a thermal refraction [7]. We used an output pulse from an optical parametric amplifier (OPA) with sum-frequency mixing, generated by an idler light and a residual input pump laser. The wavelength was tuned over a wide visible range of 540–610 nm around the surface plasmon resonance. The focal length of the lens was 60 mm. The beam waist at the focal point of the apparatus was about 20 μm. The maximal peak intensity on the spot was 8×10^{11} W/cm^2. All the optical experiments were carried out at room temperature.

3. Results and discussion

Steady-state absorption spectra of Cu nanoparticle composites in transparent substrates with various refractive indices are shown in Fig. 1. An absorption peak around 2 eV is due to the surface plasmon resonance and results from formation of Cu nanoparticles in the substrates. The steep rise in absorption around 3 eV corresponds to the optical energy gap, which is 3.2 eV for $SrTiO_3$, and 3.0 eV for TiO_2. The surface plasmon peak shifts to red and is enhanced with increasing refractive index of the substrate. Optical absorption spectrum of a metal nanoparticle composite is expressed by:

$$\alpha = p\frac{\omega}{n_0 c}|f_l|^2\varepsilon''_m, \tag{1}$$

where p is the volume fraction of the metal nanoparticles, n_0 denotes the linear refractive index, c and ω represent the velocity and frequency of light, respectively [1]. The

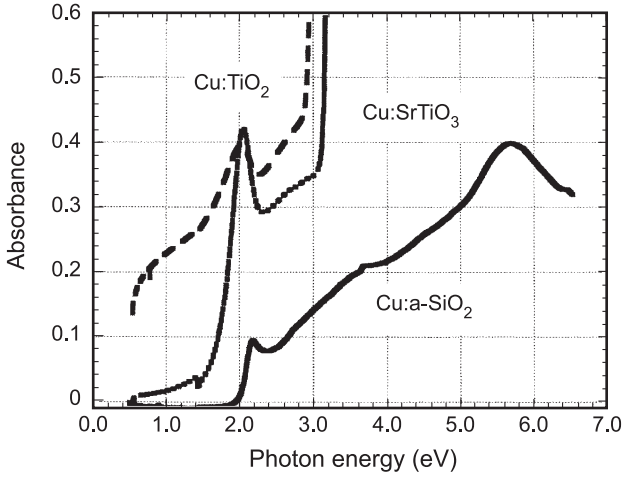

Fig. 1. Steady-state absorption spectra of Cu nanoparticle composites fabricated into a-SiO_2, $SrTiO_3$ and TiO_2 by negative ion implantation with a total dose of 1×10^{17} ions/cm^2.

imaginary part of the dielectric constant of metal nanoparticle, ε''_m and the local field factor, f_l, dominate the surface plasmon resonance. The local field factor is the ratio between the internal field and the external field and is given in Maxwell-Garnett approximation by

$$f_l = \frac{3\varepsilon_d(\omega)}{\varepsilon_m(\omega)+2\varepsilon_d(\omega)}. \tag{2}$$

Here, $\varepsilon_d(\omega)$ and $\varepsilon_m(\omega)$ present the complex dielectric constants of matrix substrate and metal nanoparticle, respectively. The local field factor depends on not only the metal particle but also the substrate matrix. Fig. 2 shows numerical calculations of $|f_l|^2$ spectra for a Cu nanoparticle in a-SiO_2, $SrTiO_3$ and TiO_2. The dielectric constants of the matrices used are evaluated by spectroscopic ellipsometry. Here, the dielectric constant of Cu nanoparticles used includes a size effect through the mean free path of collisions between free electrons in the Drude model, where the radius of Cu nanoparticle is 10 nm [15]. The imaginary part of the dielectric constant of bulk Cu and the two contributions, which consist of free electron and interband contributions, are shown in Fig. 2 as a reference. The imaginary part reflects the joint density of state. The resonance peak of the Cu:a-SiO_2 composite overlaps with the interband transition of the *d* band to the *sp* bands and attenuates due to the overlapping. However, with increasing dielectric constant of the matrix substrate, the resonance frequency deviates from the interband transitions with red shift and the peak intensity is enhanced. Absorption spectra as shown in Fig. 1 reflect the enhanced factor. The peak intensity of the Cu:TiO_2 composite shows broader and weaker structure than that of the Cu:$SrTiO_3$ composite and the calculation. The weak resonance peak may be due to scarce formation of nanoparticles and irradiation damage in the substrate.

The metal nanoparticle composites show large optical nonlinearities defined by a third-order optical susceptibility