Microstructure and optical absorption property of the Cu/SiO₂ nano-films

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1. Introduction

Metal nanoparticles embedded in dielectric matrices are stimulating the interest of scientists because of their linear and nonlinear optical properties. The interest is driven by the large number of potential applications such as optical computing, optical correlators and optical modulators [1,2]. Their optical response arises from the excitation of surface plasmons in the metal nanoparticles, due to the dielectric confinement effect of the free electrons in the metal nanoparticles [3,4]. In nanocomposite systems, a strong local field effect arises primarily from the dielectric confinement effect and shows a maximum at the surface plasmon resonance (SPR) frequency. In general, the frequency of SPR depends on both the dielectric properties of the metal and the embedding medium, as well as the size, size distribution and shape of the nanoparticles [5–7]. One of the future candidates to produce nonlinear optic devices are nanocomposite systems made of noble metal nanoparticles embedded in a dielectric matrix, e.g. silica which has been widely investigated for the development of integrated optical devices with controllable nonlinear properties [8–10]. Also, it has been used for their fast response and strong nonlinear absorption [11]. Amongst the nanoclusters studied by earlier researcher, nonlinear absorption and nonlinear refraction were found to be higher in copper and copper containing nanomaterials [12–14]. For example, Battaglin et al. [12] synthesized a composite glass made of metallic copper nanoparticles embedded in silica by radio-frequency cosputtering of silica and copper, and measured the nonlinear refractive index of thin films by the Z-Scan technique. Haglund et al. [13] synthesized a copper nano-cluster composite by implanting copper ions in a fused silica and described the picosecond nonlinear optical response of the copper–dielectric composite. Although lots of efforts have been done on the copper nanoparticle composites embedded in silica, the microstructure and optical absorption properties of Cu/SiO₂ thin films prepared by a sol–gel method have not been described fully. A lot of techniques such as electrochemical deposition [15], ion implantation [16], sol–gel [17–20] and sputtering [7,21–23] have been used to prepare the composite systems of metal nanoparticles and dielectric matrices. Among above methods, sol–gel has several advantages such as high purity, ultrahomogeneity, low processing temperatures. In the present study, Cu particles dispersed SiO₂ composite thin films were prepared by a sol–gel method. The microstructure and optical absorption properties of the Cu/SiO₂ composite films were investigated with a special emphasis on the influences of Cu content.

2. Experimental

The Cu/SiO₂ thin films were prepared by a sol–gel spin-coating method. Tetraethyl orthosilicate (Si(OC₂H₅)₄, TEOS) and copper nitrate (Cu(NO₃)₂·3H₂O) were used as raw materials, and absolute ethyl alcohol (CH₃CH₂OH) as a solvent. Molar ratio of TEOS: CH₃CH₂OH: H₂O (distilled water) was 1:15:5. TEOS, CH₃CH₂OH and H₂O were mixed and stirred for 1 h at room temperature. Several drops of nitric acid were added before stirring as hydrolysis catalysis. Cu(NO₃)₂·3H₂O was added into the precursor solution with molar ratios of Cu/(Cu + SiO₂) = 5%, 10%, 15%, 20%, 25%, 30% and 35% followed by stirring for 1 h. A transparent and dark-blue Cu/SiO₂ precursor solution was obtained.