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Optical properties of ion-beam-synthesized Au nanoparticles in SiO_2 matrix

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ABSTRACT

In recent years, gold (Au) nanoparticles have been synthesized via various methods and used in optical and biomedical detection. Au nanoparticles contain some remarkable dimension-dependent optical properties due to surface plasmon resonance (SPR) in Au nanoparticles which causes high absorption in visible light regions. Since SPR in well-crystallized Au nanoparticles can enhance the local electromagnetic field, it is thus expected that greater efficiency in the photoluminescence (PL) originating from oxygen deficiency centers (ODC) can be achieved in Au-implanted SiO_2 matrix. In order to demonstrate the enhancement of PL, Au nanoparticles were formed in SiO_2 film using ion beam synthesis and their optical and microstructural properties were also investigated in this study. The results revealed that a clear absorption peak at approximately 530 nm was identified in the UV-Vis spectra and was attributed to SPR induced by Au nanoparticles in SiO_2. The SPR of Au nanoparticles is also dependent on thermal treatment conditions, such as post-annealing temperature and ambient. The Au nanoparticle-containing SiO_2 film also displayed several distinctive peaks at approximately 320, 360, 460, and 600 nm in the PL spectra and were found to be associated with ODC-related defects and non-bridging oxygen hole centers (NBOHC) in SiO_2. In addition, the PL peak intensities increased as post-annealing temperature increased, a finding contradictory to the defect recovery but highly consistent with the SPR tendency. A maximum PL emission was achieved when the Au-implanted SiO_2 film was annealed at 1100 °C for 1 h under N_2. Therefore, the existence of Au nanoparticles in SiO_2 film can induce SPR effects as well as enhance PL emission resulting from defect-related luminescence centers.

1. Introduction

The fabrication of composite glass (i.e., dielectric matrix that contains metallic nanoparticles) is one of the key issues in applications in the optoelectronic, photonic, and plasmonic fields. Numerous methods are currently being adopted to fabricate such composite materials. In order to synthesize nanoparticles that are manageable in terms of their size, shape, and depth distribution, ion beam synthesis is a promising method of forming metallic nanoparticles in solids due to its excellent spatial controllability through its adjustable implantation energy and ion fluence [1–4].

Nanostructures have received increasing attention in the past decade due to their unique properties which differ significantly from those of the corresponding bulk material. In particular, gold (Au) nanoparticles embedded in dielectric materials have received great attention due to their superior optical features resulting from the local surface plasmon resonance (SPR) phenomenon which can't be observed easily in the bulk phase. The related extinction band is predominantly caused by a collective oscillation of conduction electrons in Au nanoparticles experiencing optical excitation and thus can be characterized as a localized SPR band. Also, SPR energy levels can easily be adjusted by changing the size, shape, and environment of the Au nanoparticles [5,6].

SPR in Au nanoparticles presents promising applications in technologies such as molecular detectors, biosensors, and surface enhanced Raman scattering (SERS) [7,8]. Furthermore, SPR may enhance photoluminescence [9–14] or the band emission of the

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nanorod structure [15–17] due to the existence of Au nanoparticles. Previous studies have reported that in ion-implanted SiO_2 matrix, some defects evolve during the ion implantation process. Some of these defects, such as oxygen-deficiency centers (ODC) [18,19,22] and non-bridging oxygen hole centers (NBOHC) [20,21], are radiative, thus resulting in photoluminescence (PL) emission. Since the SPR of well-crystallized Au nanoparticles can enhance the local electromagnetic field, it is thus anticipated that a higher efficiency of PL originating from ODC can be achieved in Au-implanted SiO_2 matrix. Therefore, the objective of this study is to form Au nanoparticles in SiO_2 films by means of ion beam synthesis. This study also details the characteristics of the optical and microstructural properties in Au nanoparticles in order to clarify the SPR effects of Au nanoparticles and demonstrate the enhancement of SPR-induced PL in Au-implanted SiO_2 films.

2. Experiment

In this study, thermally-grown SiO_2 films 100 nm in thickness deposited on (100)-oriented n-type Si wafers were adopted as the matrix materials. Au ions extracted from a Nisshin High Voltage accelerator with an acceleration voltage of 60 kV were room-temperature implanted into the SiO_2 films at a fluence of 5×10^{16} ions/cm^2. The as-implanted specimens were each annealed at 650, 900, and 1100 °C for 1 h in both air and N_2 ambients. The UV-Vis absorption spectra of the specimens were measured by a HITACHI U-4100 spectrophotometer and performed at room temperature in wavelengths ranging from 370 to 800 nm. The PL spectra were detected by a HITACHI F-7000 fluorescence spectrophotometer which was stimulated by a 248-nm line (5 eV) from a Xe lamp with a spectral filter. X-ray diffraction (XRD) measurements were conducted using a Shimadzu XRD-6000. Spherical-aberration-corrected transmission electron microscopy (TEM) (JEOL, JEM-ARM200FTH) operating at 200 kV was used to carry out the micro-structural analysis and selected area electron diffraction (SAED) of the specimens. The TEM samples were prepared in a cross-section in order to observe depth distribution of the Au nanoparticles. The depth profiles of the Au ions were measured utilizing a TOF-SIMS IV secondary ion mass spectrometer (SIMS). Defects and binding energy levels were analyzed using a ULVAC-PHI high-resolution X-ray photoelectron spectrometer (XPS).

3. Results and discussion

In order to characterize the SPR effects caused by Au nanoparticles, the UV-Vis absorption spectra of the Au-implanted specimens annealed at various temperatures in air and N_2 ambients are shown in Fig. 1. As can be seen, a clear absorption peak around 530 nm is evident in both the air- and N_2-annealed specimens, which corresponds to the SPR peak. This is due to the presence of Au nanoparticles as predicted according to the Mie Theory [1]. The SPR peak also becomes more prominent as annealing temperature increases, implying that high-temperature annealing enhances the synthesis of Au nanoparticles as well as nanoparticle coalescence. In the specimen annealed at 1100 °C in air, a broad shoulder appears in the wavelength between 400 and 500 nm, which can be attributed to the thicker SiO_2 layer due to oxidation reaction during high-temperature air annealing. This is evident from the cross-sectional TEM images and the depth profile analysis.

Fig. 2 shows the cross-sectional TEM images and the corresponding SIMS-measured depth profiles of the as-implanted, air-annealed, and N_2-annealed specimens. It can be seen that the maximum concentration of Au ions is located at approximately the same depth (i.e., 30 nm) in three of the specimens. High-temperature annealing enhances the redistribution and clustering of excess Au atoms in SiO_2, thus resulting in a remarkable increase in the size of the Au nanoparticles. The air-annealed specimens especially have larger particles and narrower depth distributions when compared to the N_2-annealed specimens. It can be seen in the TEM images that air annealing at 1100 °C for 1 h leads to an Au particle size with a diameter of about 10–15 nm, while the specimens annealed in N_2 at the same temperature and for the same duration have diameters of less than 10 nm. This variation in particle size in these two annealing ambients is caused by the differing diffusivity of Au atoms in the SiO_2 matrix. This phenomenon was mentioned by De Marchi et al. [1,2], who claim that Au atoms prefer clustering when undergoing annealing in an aerobic environment. The incorporation of oxygen can promote the diffusion of Au atoms as well as enhance the growth of Au nanoparticles. Therefore, the annealing ambient is an important factor in the synthesis process of Au nanoparticles. Fig. 3 (a) and (b) show the XRD spectra of the Au-implanted specimens annealed in air and N_2, respectively. Given the specific diffraction peaks shown in Fig. 3, the mean size of the Au nanoparticles annealed in different annealing atmospheres can be estimated according to the Scherrer equation given below,

$$\tau = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where, τ is the mean size of the ordered (crystalline) domains, K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line which broadens at halfway point to the maximum intensity (FWHM), and θ is the Bragg angle. The shape factor, incident wavelength, and Bragg angle are the constants in this experiment. In regard to the relationship between the mean size factor τ and the FWHM β, the spectra clearly show that when the temperature is increased, larger Au nanoparticles are produced. A narrower FWHM indicates a larger average particle size in air annealing when

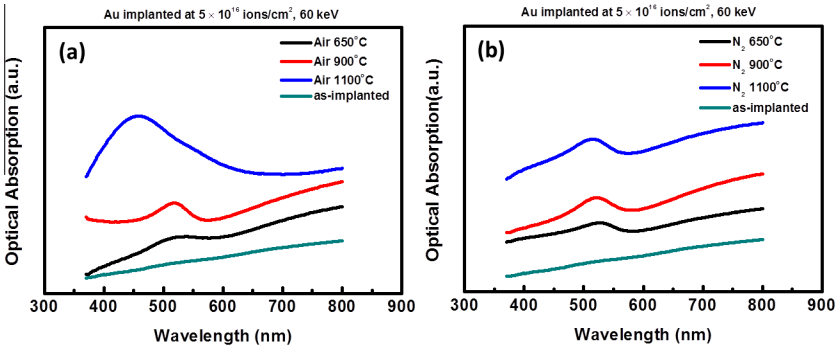

Fig. 1. Optical absorption spectra of Au-implanted specimens annealed in (a) air, and (b) N_2 for 1 h.