Introduction

Noble metal nanoparticles strongly adhered on the dielectric matrices have been extensively studied because of their pronounced applications in optical devices based on tunable localized surface plasmon resonance (LSPR) absorption band. To develop optical devices by using LSPR, it is important to establish a method to disperse noble metal nanoparticles homogeneously on dielectric substrates and to tune the wavelength of LSPR. Compared with chemical synthesis methods, the noble metal nanoparticles formed by ion irradiation on the dielectric substrate draw significant interest in recent years because of the distinct optical properties due to homogeneous single layer dispersion of noble metal nanoparticles and no requirement of interlayer deposition on dielectric substrates. However, the investigation of noble metal nanoparticles’ microstructure in the dielectric substrate and their relationship with the optical property have been rarely conducted. Therefore, a detailed investigation of ion irradiation induced surface nanostructuring and their optical properties of noble metal films on dielectric substrates were conducted in this doctoral thesis.

Experimental procedure

Firstly, Au, Ag, Ag–Au bimetallic thin films were thermally evaporated on mirror polished SiO\textsubscript{2} amorphous substrate and Al\textsubscript{2}O\textsubscript{3} single crystal (viz. sapphire) substrate at ambient temperature under a 6.0 × 10\textsuperscript{−5} Torr vacuum. The film thickness was verified by cross–sectional transmission electron microscope (TEM; JEOL JEM–2010F), and a field–emission scanning electron microscope (SEM; JEOL JSM–7001FA) equipped with an energy–dispersive spectrometer (EDS) was used to measure the composition of deposited film and to examine the surface morphology.

100 keV Ar\textsuperscript{+}–ion irradiations at ambient temperature with various fluences were performed to study the fluence dependence. Energies of the ions have been chosen such that the range is wider than the thickness of the metal layer, as calculated by the SRIM 2011 code. Ar\textsuperscript{+}–ion irradiation on the specimen was performed using the 400 keV ion accelerator at High Voltage Electron Microscope Laboratory, Hokkaido University. A low pressure of 10\textsuperscript{−3} Pa was maintained inside the irradiation chamber. To ensure uniform irradiation, Ar\textsuperscript{+}–ions beam was scanned and the current was maintained at approximately 2.0 μA cm\textsuperscript{−2}. After irradiation, thermal annealing was conducted ex–situ in high vacuum (4.25 × 10\textsuperscript{−5} Pa) at 773 K for two hours.

After that, optical absorption spectra were recorded over a wavelength range of 300–800 nm on a spectrophotometer (JASCO V–630) with a spectral bandwidth of 1.5 nm, and the SEM observations were conducted to examine the surface modification. The line and surface elemental concentration were evaluated in the nanoscale using SEM coupled with an EDS. Linear chemical concentration profile cross the surface was obtained using the SEM operated at 6.0
keV. Moreover, microstructural characterization was performed using the TEM operated at 200 keV. Cross-sectional TEM specimens were prepared using a precision ion polishing system (PIPS; JEOL AT–12310), and ion milling was performed using a cold stage to avoid undesired thermal modification of the samples. Also, a focused ion beam facility (JEOL JEM–9320FIB) was used to prepare the cross-sectional TEM specimens.

**Results and Discussions**

■ Ion Beam Surface Nanostructuring of Thin Au Film on SiO$_2$ Glass

Ion–beam induced surface nanostructuring and the burrowing of the nanostructures by the Ar$^+$–ion irradiation are described. 100 keV Ar$^+$–ions were irradiated to SiO$_2$ substrate with 30 nm gold film on the surface with various fluences. The surface morphologies were investigated by AFM and SEM. Dewetting of Au thin films due to radiation–enhanced diffusion were observed. At the same time, the burrowing of the nanostructures into dielectric matrix was observed. The burrowing of these nanostructures was verified by cross sectional microstructure observation by TEM. Finally, a single layer of spherical Au nanoparticles deeply embedded in the SiO$_2$ substrate was obtained. The LSPR absorption band due to the localized surface plasmon excitation of these Au nanoparticles was also confirmed by photo absorption spectra. In addition, the dependence of the LSPR absorption band on ion beam energy was studied and a shift of the absorption band towards the longer wavelength (red shift) with the increase of ion beam energy was obtained.

■ Ion Beam Surface Nanostructuring of Ag–Au Bimetallic Films on SiO$_2$ Glass

The control of various parameters sensitive to the LSPR absorption band (including particle size and shape) by irradiation fluence was described. Experimentally, 100 keV Ar$^+$–ion irradiation of 30 nm Au$_{5050}^{}$–Ag$_{5050}^{}$ films deposited on the SiO$_2$ glass substrate was conducted. By increasing the irradiation fluence, the mean size of the nanospheroids decreased, the aspect ratio approached unity and the satellite nanoparticles were formed. It resulted in a shift of the LSPR absorption band towards the shorter wavelength up to an irradiation fluence of $1.0 \times 10^{17}$ cm$^{-2}$. The peak was then shifted towards longer wavelength with further irradiation and the multi–sphere scattering effects due to the satellite nanoclusters was proposed to accounts for this absorption band shift. Further control of LSPR absorption band over a wider range has been achieved by synthesizing Ag–Au bimetallic nanoparticles fabricated in the form of alloys. Experimentally, 100 keV Ar$^+$–ion irradiation of 30 nm pure silver, pure gold, and three different bimetallic Ag–Au films on SiO$_2$ substrate have been conducted, and a single layer photosensitive Ag–Au bimetallic nanoparticles embedded in a SiO$_2$ substrate was obtained. A remarkable LSPR peaks shifted towards the longer wavelength with the increase of the Au concentration was obtained. Gans theory has been used to model the LSPR absorption band of these metallic nanoparticles embedded in SiO$_2$ substrates. This theory accounts for the main effects associated with the major behaviors of the localized surface plasmon excitation.

■ Ion Beam Surface Nanostructuring of Ag–Au Bimetallic Films on Sapphire

LSPR absorption band’s dependence on substrate structure was investigated by use single crystal Al$_2$O$_3$ substrate. The process of ion irradiation induced surface nanostructuring of 30nm Au–Ag bimetallic films on single crystal Al$_2$O$_3$ substrate was different from that on the amorphous SiO$_2$ substrates due to the substrate structure difference. In case of single crystal Al$_2$O$_3$ substrate, higher fluence of $3.8 \times 10^{16}$ cm$^{-2}$ (in this study) was required to make the near surface amorphous. Therefore, ion irradiation can sufficiently increase the ion-induced viscous flow to burrow Au–Ag bimetallic nanoparticles into single crystal
Al₂O₃ substrate. This further supported the present mechanism for the ion induced burrowing of rigid nanoparticles into viscous media. In addition, dependence of the LSPR absorption band on the gold concentration was also observed; however, the tendency is diverted away from the tendency on the amorphous SiO₂ substrate.

Conclusions

In this study, 100 keV Ar⁺–ion irradiation on thin metallic film deposited dielectric substrates was employed. Ion–beam induced surface nanostructuring were investigated by AFM and SEM. Further irradiation effectively initiate the burrowing of the nanostructures into dielectric matrix, as the ion–induced viscous flow is sufficient enough to accomplish this burrowing process. This was verified by cross sectional microstructure observation and chemical characterization obtained by TEM equipped with an EDS. Finally, their optical responses were evaluated by photo absorption spectra, obtained by a double beam spectrophotometer, and the characteristic LSPR band was observed for the metallic nanoparticles. In addition, the synergistic control of various parameters sensitive to the LSPR band includes both particle size and shape, which was realized by modifies the ion beam current, energy, fluence, and also the metallic film thickness. Further control of LSPR frequency over a wider range has been achieved by synthesizing bimetallic nanoparticles fabricated in the form of alloys of two metals.

Publications