学 位 論 文 内 容 の 要 旨

DISSERTATION ABSTRACT

博士の専攻分野の名称　博士（工学）　氏名　蒙　萱

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Ion beam surface nanostructuring of metallic thin films on dielectric substrates and their optical properties

(イオンビームによる金属薄膜/誘電体表面のナノ構造化とその光学特性)

In the past decade, metallic nanoparticles either sustained on the surfaces or dispersed in dielectric matrices have been extensively studied experimentally as well as theoretically because of their pronounced optical and electrical properties. Materials under ion irradiation undergo significant atomic rearrangement and this process effectively introduces surface nanostructuring on the dielectric surface. However, there is the unsolved issue as follows: the nanoparticles microstructure and optical property dependence on ion irradiation parameters.

Chapter 1 gives a brief review of the potential application of nanoparticle sustained on dielectric substrate. Then a brief introduction of the ion beam irradiation induced surface nanostructuring was given. Finally, the main purposes of this thesis are highlighted: (a) to investigate the nanoparticles microstructure dependence on ion irradiation parameters and (b) to investigate the optical properties dependence on the nanoparticles morphology.

Chapter 2 gives a description of experimental procedures. The specimen preparation, ion irradiation condition, and the characterization methods including spectrophotometry, atomic force microscopy (AFM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were described in detail.

In Chapter 3, 100 keV Ar^+ion irradiation with fluences from $1.0\times10^{16}cm^{-2}$ to $1.0\times10^{17}cm^{-2}$ on 30 nm Au film deposited SiO_2 substrate was conducted. Ion beam induced surface nanostructruring were investigated by AFM and SEM. Ion irradiation enhanced dewetting of Au thin films due to radiation enhanced diffusion were observed. Further irradiation effectively initiate the burrowing of the nanostructures into dielectric matrix, and the ion-irradiation induced viscous flow is accounted for this burrowing process. This was verified by cross sectional microstructure observation by TEM operated in the scanning mode equipped with an energy-dispersive spectrometer (EDS). Finally, a single layer Au nanoparticles with spherical shape deeply embedded in the SiO_2 substrate was obtained and their optical responses were evaluated by photo absorption spectra. The enhanced absorption band was observed and is ascribed to be the localized surface plasmon excitation of these Au nanoparticles. In addition, an increase of the lattice expansion was observed with irradiation fluence. These lattice expansions could be caused by irradiation induced lattice defects and the irradiation induced interface ion-mixing. Also, 150 keV Ar ion irradiaiton of 30 nm Au film on SiO_2 substrate with a fluence of $1.0\times10^{17}cm^{-2}$ was conducted, and a shift of the localized surface plasmon resonance (LSPR) ab-

sorption band towards the longer wavelength (red shift) was obtained, which was ascribed to be the increase of the Au nanoparticles with the increasing of ion beam energy.

In chapter 4, the control of various parameters sensitive to the LSPR absorption band includes particle size and shape, which can be realized by modifies the ion beam energy and irradiation fluence. Therefore, 100 keV Ar^+ irradiation of 30 nm $Ag_{50\%}$-$Au_{50\%}$ films deposited on the SiO_2 glass substrate was conducted. As the irradiation fluence increases from $4.0\times10^{16}cm^{-2}$ to $1.4\times10^{17}cm^{-2}$, the mean size of the nanospheroids decreases and the aspect ratio approaches unity with an increase in the irradiation fluence, resulting in a shift of the LSPR peaks towards the shorter wavelength up to an irradiation fluence of $1.0\times10^{17}cm^{-2}$. The peak was then shifted towards the longer wavelength. Cross-sectional TEM image showed satellite nanoclusters surrounding the core spheroid after ion irradiation, and these satellite nanoclusters may have a contribution to this shift. 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. Experimentally, 100 keV Ar-ion irradiation of 30 nm pure silver, pure gold, and three different bimetallic Ag-Au films with molar ratios of 0.25:0.75, 0.5:0.5, and 0.75:0.25 deposited on SiO_2 substrate was conducted, and a single layer of photosensitive Ag-Au bimetallic nanospheroids embedded in a SiO_2 substrate was obtained. In addition, a remarkable LSPR peaks shifted approximately linearly towards the longer wavelength with the increase of the Au concentration has been obtained.

Gans theory has been used to model the optical response of these metallic nanospheroids embedded in SiO_2 substrates. This theory accounts for the main effects associated with the major behaviors of the localized surface plasmon excitation. However, the Gans predictions is underestimated the experimental results. Two other effects should be taken into consideration, firstly, the strong coupling between the core nanospheroid and the satellite nanoclusters due to ion irradiation; secondly, the increase of the dielectric function of SiO_2 matrix due to the metallic atoms recoiled into the SiO_2 matrix. Both effects will have a contribution by producing a red shift of the LSPR absorption band.

In chapter 5, substrate effect was investigated by use sapphire single crystal substrate. The process of ion irradiation induced surface nanostructuring of 30nm Au-Ag bimetallic films on sapphire substrates was compared with that on the amorphous SiO_2 substrates. It is obvious that dewetting pattern as well as the embedment process were quite different. For the sapphire substrate, a higher fluence $3.8\times10^{16}cm^{-2}$ in my study is required to make the near surface amorphous, and therefore to sufficiently increase the ion-induced viscous flow to start the burrowing of Au-Ag bimetallic nanoparticles into sapphire substrate. In addition, dependence of the LSPR absorption band on the chemical concentration was also observed; however, the tendency is diverted far away from the tendency on the SiO_2 glass substrate. Metallic nanostructure formation strongly depends on surface structure of substrate.

Chapter 6 is the conclusion of all these studies. Based on the aforementioned results, ion irradiation is an effective approach in surface nanostructuring and in controlling the LSPR properties of the metallic films on dielectric substrates, and the application of these nanocomposites in solid-state devices is expected.