Optical constants and their dispersion of Ag-MgF_2 nanoparticle composite films

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Ag-MgF_2 composite films with different Ag fractions were prepared through a co-evaporation method. Microstructure analysis shows that the films are composed of amorphous MgF_2 matrix and embedded fcc-Ag nanoparticles. The optical constants and their dispersion of the films, within the wavelength range of $250-650$ nm, were measured by reflecting spectroscopic ellipsometry. The maximum of the imaginary part ε'' of the complex dielectric permittivity attributing to the surface plasmon resonance polarization of the Ag nanoparticles in an Ag-MgF_2 film, and the tangent of the phase-shift angle δ resulting from the dielectric loss of the film, occur at $\lambda = 435$ nm and $\lambda = 420$ nm, respectively. Based on Maxwell-Garnett effective medium theory, the experimentally observed dispersion spectra were reasonably described.

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Optical constants are important physical quantities to characterize the macroscopic optical properties of solids. Both complex refractive index $N = n + ik$ and complex dielectric permittivity $\varepsilon = \varepsilon' + i\varepsilon''$ are optical constants since they can be related through general Maxwell relation $N = \sqrt{\varepsilon}$[1]. Actually, all above "constants" are the functions of the frequency of incident light. The frequency dependence of optical constants is called dispersion.

As both Ag and MgF_2 are important electrical and optical materials, a number of detailed studies concerning their properties, i.e. reflectivity, transmittance, refractive index, extinction coefficient etc., have been made[2−6], and much attention has been paid to the direct applications of Ag and MgF_2 in virtue of their distinct properties. However, only a few studies[7] have been made for Ag-MgF_2 composite films which should possess interesting properties.

For years, our group has been studying the preparation, microstructure, and properties of Ag-MgF_2 composite films. Some significant results, especially those concerning the optical and electronic properties of nanoparticle Ag-MgF_2 composite films which make it possible to employ an Ag-MgF_2 composite film as a promising candidate for photoelectronic devices, have been achieved[8−13]. This paper reports the experimental and theoretical results of the optical constants and their dispersion of Ag-MgF_2 composite films.

To approximate film composition to evaporant composition, in-vacuum-sintered Ag-MgF_2 mixture was used as evaporant. The composite evaporant was prepared as follows: metal and dielectric powders, in the designed proportions and both with a purity of 99.99%, were thoroughly mixed, ground and pressed into tablets at a pressure of 600 kg/cm^2. Then the tablets were sintered under N_2 protection at 900 °C for one hour. After sintering, the tablets were ground into fine granules to be collected as evaporant. Monitored by a quartz oscillator, Ag-MgF_2 composite films of about 300-nm thickness were prepared by conventional vapor deposition onto Si(111) substrates at 80 °C and in a base vacuum better than 10^{-4} Pa. After the deposition, the films were heat-treated at 350 °C for 40 minutes in a vacuum of 10^{-3} Pa.

An RAP-I type fully automatic spectroscopic ellipsometer was employed to determine the dependence of the complex dielectric permittivity $\varepsilon = \varepsilon' + i\varepsilon''$ of Ag-MgF_2 composite films on the incident wavelength λ in the wavelength range of $250-650$ nm. A JEM-100SX type transmission electron microscope (TEM) and a Y-4Q type X-ray diffractometer (XRD) were used to analyze the microstructure of Ag-MgF_2 composite films. The microstructure analysis results suggested that the films be composed of amorphous MgF_2 matrix and embedded fcc-Ag nanoparticles with a mean size of about $15-18$ nm[9,12,13].

The experimental spectra, by reflecting ellipsometry, of the complex dielectric permittivity $\varepsilon = \varepsilon' + i\varepsilon''$ of a composite film with moderate Ag fraction (15 vol.-% Ag-MgF_2) are shown in Fig. 1. The real part ε' of the complex dielectric permittivity reaches its

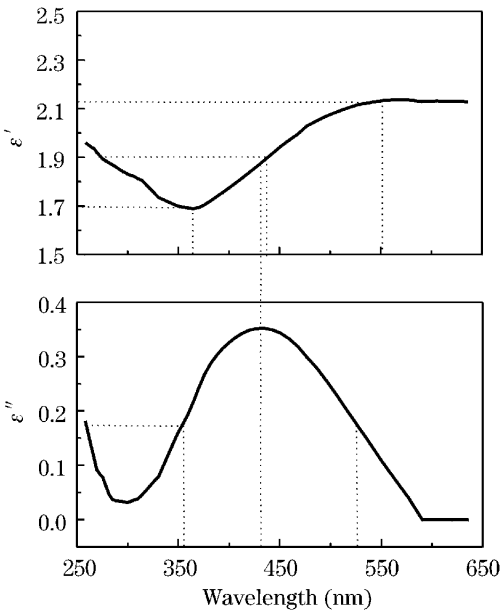

Fig. 1. Experimental spectra of ε' and ε'' versus λ.

maximum $\varepsilon'_{max} = 2.13$ at $\lambda'_1 = 551$ nm and arrives at its minimum $\varepsilon'_{min} = 1.69$ at $\lambda'_2 = 364$ nm. The corresponding wavelength λ'_0 of the value $(\varepsilon'_{max} + \varepsilon'_{min})/2 = 1.91$ is 438 nm. Therefore, $\Delta\lambda' = \lambda'_1 - \lambda'_2 = 187$ nm corresponds to the abnormal dispersion region of ε'. The imaginary part ε'' of the complex dielectric permittivity reaches its maximum $\varepsilon''_{max} = 0.35$ at $\lambda''_0 = 435$ nm, which is close to λ'_0. The wavelengths $\lambda''_1 = 527$ nm and $\lambda''_2 = 354$ nm, corresponding to the two section points of the surface plasma resonance (SPR) polarization peak of Ag nanoparticles in ε'', can be determined from $\varepsilon''_{max}/2 = 0.175$. The peak width at half height of the SPR peak is thus $\Delta\lambda'' = \lambda''_1 - \lambda''_2 = 173$ nm, which is 14 nm less than $\Delta\lambda'$. Comparing the abnormal dispersion region in ε' with the resonance polarization region in ε'', it is found that the resonance polarization peak shifted about 3 nm towards the short-wavelength side. From the relation between ε' and wavelength, it is obvious that within the range of $\Delta\lambda'$ the real part ε' increases as wavelength increases, while in the other range ε' decreases as wavelength increases. The former falls into the category of abnormal dispersion and the latter attributes to the normal dispersion. Both of these two kinds of dispersion are right the characteristics of electron displacement polarization.

According to the theory of dielectrics, the tangent of the phase-shift angle δ resulting from dielectric loss can be determined by

$$\mathrm{tg}\delta = \frac{\varepsilon''}{\varepsilon'}. \tag{1}$$

By using the obtained ellipsometry data of the complex dielectric permittivity ε' and ε'', $\mathrm{tg}\delta$ as a function of λ is calculated and presented in Fig. 2. The maximum of the tangent of the phase-shift angle δ appears at $\lambda = 420$ nm. Comparing the peak location of $\mathrm{tg}\delta$ with those of k and ε'', there exists a blue shift of 15 nm.

Our studies on the microstructure of Ag-MgF_2 composite films confirmed that it is valid to apply Maxwell-Garnett theory to explain the optical properties of the films. According to the theory[14], the complex dielectric permittivity $\varepsilon(\lambda)$ of an Ag-MgF_2 composite film is given by

$$\frac{\varepsilon(\lambda) - \varepsilon_D(\lambda)}{\varepsilon(\lambda) + 2\varepsilon_D(\lambda)} = q\left(\frac{\varepsilon_M(\lambda) - \varepsilon_D(\lambda)}{\varepsilon_M(\lambda) + 2\varepsilon_D(\lambda)}\right), \tag{2}$$

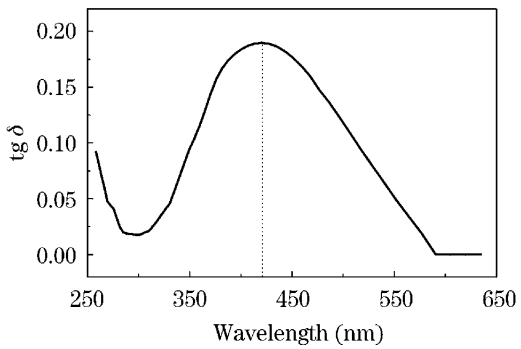

Fig. 2. Tangent of the dielectric loss angle δ versus incident wavelength λ.

where $\varepsilon_M(\lambda)$ and $\varepsilon_D(\lambda)$ denote the complex dielectric permittivity of the metal particles and the dielectric matrix, respectively, and q is the volume fraction of the metal component in the film. From the relation between complex dielectric permittivity and complex refractive index

$$\varepsilon(\lambda) = \varepsilon'(\lambda) + i\varepsilon''(\lambda) = (n + ik)^2, \tag{3}$$

the extinction coefficient k of a composite film can be written as

$$k = \frac{1}{\sqrt{2}}\{\sqrt{[\varepsilon'(\lambda)]^2 + [\varepsilon''(\lambda)]^2} - \varepsilon'(\lambda)\}^{1/2}. \tag{4}$$

In terms of Eq. (2), the complex dielectric permittivity $\varepsilon(\lambda)$ of Ag-MgF_2 composite films ($q = 0.05$, 0.10, 0.15, 0.20, and 0.30) were calculated and plotted in Figs. 3(a) and (b). In the calculation, Palik's complex dielectric permittivity data[4] for Ag and MgF_2 were adopted. From the ε'' curve for the film with $q = 0.15$ in Fig. 3(b), the maximum of the imaginary part ε'' appears at $\lambda = 427$ nm. By making a comparison between the two profiles of the theoretical and experimental ε'' spectra, it can be found that there are an obvious broadening and a red-shift of 8 nm for experimental SPR polarization peak. The broadening and the red-shift could be resulted due to the difference of the size and the shape of the metal nanoparticles in an actual Ag-MgF_2 composite film[12].

By applying $\varepsilon'(\lambda)$ and $\varepsilon''(\lambda)$ obtained from Maxwell-Garnett formula to Eq. (4), the extinction coefficient k of the film with $q = 0.15$, as a function of λ, is evaluated and shown in Fig. 4. The peak of k is located at $\lambda = 427$ nm, which is right the result of SPR absorption of Ag nanoparticles in the film.

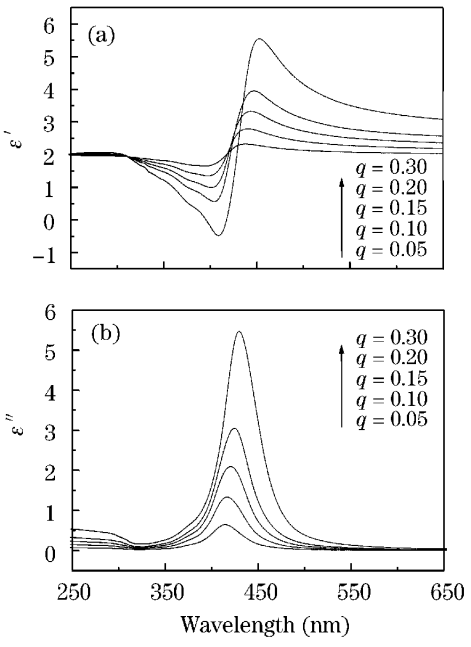

Fig. 3. Theoretical $\varepsilon(\lambda)$ of Ag-MgF_2 composite films with different q. (a) Real part $\varepsilon'(\lambda)$; (b) imaginary part $\varepsilon''(\lambda)$.

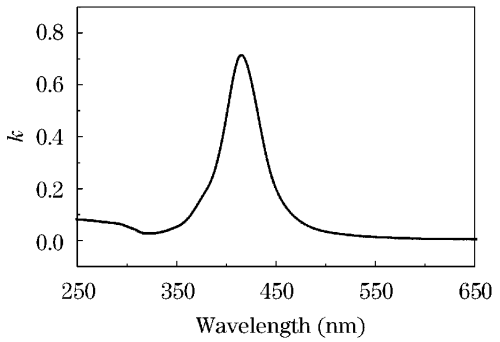

Fig. 4. Theoretical extinction coefficient k of Ag-MgF_2 composite film ($q = 0.15$) versus wavelength λ.

In conclusion, Ag-MgF_2 composite films with different Ag volume fractions were prepared by co-evaporation deposition. The dependence of the complex dielectric permittivity $\varepsilon = \varepsilon' + i\varepsilon''$ of Ag-MgF_2 composite film on the incident wavelength λ in the range of $250 - 650$ nm was experimentally studied in detail by employing reflecting spectroscopic ellipsometry. The maximum of the imaginary part ε'' of the complex dielectric permittivity attributing to the SPR polarization of embedded Ag nanoparticles in the film, and the tangent of the phase-shift angle δ resulting from the dielectric loss of the film, occur at $\lambda = 435$ nm and $\lambda = 420$ nm, respectively. Based on Maxwell-Garnett effective medium theory, the experimental $\varepsilon = \varepsilon' + i\varepsilon''$ spectra were reasonably described.

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