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Optical constants of long silver nanowire thin films on glass calculated from the transmission spectra

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ABSTRACT

Silver nanowire thin films are a promising material for an application in optoelectronic and photonic devices. The refractive index is one of the most fundamental optical properties, yet for silver nanowire films it has not been studied so far. In this study, long silver nanowires (L-Ag NWs) were synthesized via a polyol-based thermal method and then spin-coated onto glass substrates. The optical transmittance properties of L-Ag NW thin films were characterized by UV–VIS spectrometry, refractive index, dielectric coefficient of the L-Ag NW films were determined from the transmittance and reflectance data. The results show that the refractive index of the L-Ag NW film remains nearly constant over a wide wavelength range, whereas the extinction coefficient first decreased and then subsequently increased.

1. Introduction

Transparent electrodes based on tin-doped indium oxide (ITO) have been extensively used as electrodes in touch panels, light-emitting diodes and thin film solar cells [1,2]. Typically, ITO is prepared through expensive physical vapor deposition processes. Furthermore, indium is a scarce and expensive resource [3]. Thus, in industry, there is an increasing need for new transparent conductive materials with a lower fabrication cost than ITO. Ag nanowires (NWs) [4,5] have recently received a lot of attention as a potential replacement for ITO in optoelectronic devices [6]. However, the optical properties of Ag NWs films have so far not been sufficiently discussed in the literature.

The refractive index of Ag NWs film is an equally important yet unstudied parameter which must be known for a successful application. Unlike other thin films, silver NW films consist of discrete nanowires. Thus, the film thickness varies significantly throughout the 2-D plane, and the Ag NW films show the structural characteristics of mesh films. The optical properties of Ag NW film exhibit a greater uncertainty and are affected by the processing parameters. As a result, it is difficult to reliably determine the optical index. Furthermore, the optical properties of nano-scale materials are affected by adjacent media, i.e., the properties of the NWs and the surrounding media are interdependent and interaction with each other.

In this paper, the refractive index n of long silver nanowire (L-Ag NW) films deposited on glass was investigated. The refractive indices and extinction coefficients of glass and the L-Ag NW film on a glass substrate were calculated from both reflectance and transmittance data.

2. Material and methods

The L-Ag NWs were synthesized via a polyol-based method previously reported in literature [7]. In short, PVP (0.23 g) was first dissolved in 30 ml of ethylene glycol (EG). Next, $AgNO_3$ (0.25 g) was added rapidly to the PVP solution, which was then stirred until clear. Subsequently, 3.0 g of an $FeCl_3$ solution (600 μM in EG) were added rapidly to the solution within 1 min. The reaction was allowed to proceed at 130 °C for 4 h. After cooling, the solutions were washed with ethanol and centrifuged, with the purification process being repeated 3 times. Thus the final dispersion of L-Ag NWs in ethanol was obtained. The L-Ag NW films were obtained by spin-coating the NWs on glass substrates. Afterwards, the L-Ag NW film samples were dried at 200 °C for 20 min on a hotplate.

The transmittance and reflection spectra were recorded using an UV–VIS spectrophotometer (Cary 5000, Varian Co, USA). The morphology of the films was characterized scanning electron microscopy (SEM) (SUPRA 550p, Zeiss) and X-ray diffraction

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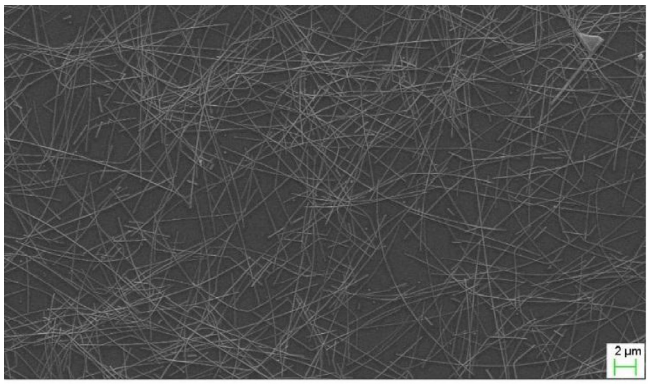
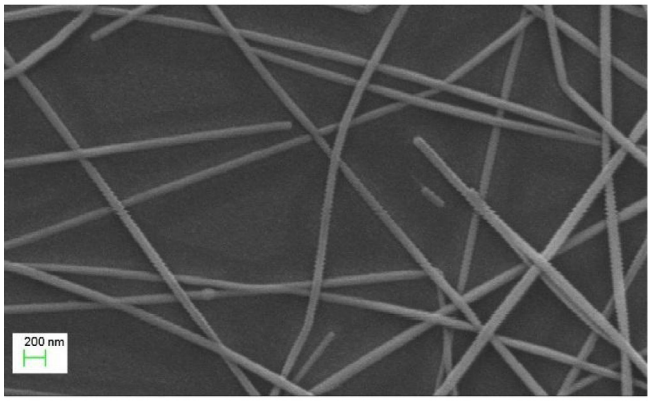
(XRD) patterns of the films were obtained using a X-ray diffractometer (DX-2700).

3. Results and discussion

As shown in Fig. 1(a) and (b), the SEM images of the L-Ag NWs reveal that the average length of the NWs is approx. 40 μm. The L-Ag NWs are uniformly distributed on the glass substrate. There is a minimal presence of nanoparticles in the films. The corresponding XRD pattern obtained for the L-Ag NWs is shown in Fig. 1(c). The peaks at 38° and 44° correspond to the (111) and (200) planes of the face-centered cubic (fcc) silver crystals (JCPDS 04-0783). No peak related to silver oxide was observed, indicating a high purity and high quality of the L-Ag NWs.



(a)



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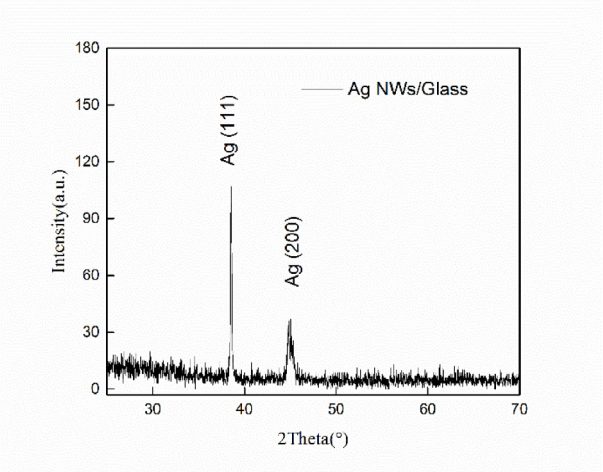

(c)

Fig. 1. SEM images (a, b) and XRD pattern (c) of Ag NWs/glass.

Fig. 2(a) and (b) show the optical transmittance and optical reflectance spectra recorded for both L-Ag NWs on glass and the bare glass substrate. The transmittance of the glass substrate over the wavelength range from 400 to 1500 nm was determined to be ~88–92%. After coating the L-Ag NWs onto the substrates, the transmittance decreased to ~77–83%. The decreased transmittance was caused by two factors: First, a back-scattering of light due to the L-Ag NWs, which also leads to an increase in reflection, as shown in Fig. 2(b). Second, the increase in absorption due to the L-Ag NWs also contributed to the decreased transmittance. The absorption of the L-Ag NWs on glass and the bare glass was calculated by the transmittance and reflectance, and the resulting values are presented in Fig. 2(c). The absorption of the glass substrate was found to be close to zero, whereas the absorption of the L-Ag NWs on glass was close to 0.1. Because in our study the thickness of the glass (1 cm) was at least about $\sim 10^6$ times over the thickness of the L-Ag NWs (diameter 100 nm), we regard almost all absorption to stem from the L-Ag NWs.

The evaluation of the refractive indices of optical materials is highly important for potential applications in optoelectronic devices [8]. The refractive index n and extinction coefficient k of the L-AgNWs on glass can be determined using the following Eqs. (1) and (2) [9,10]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{1-R^2} - k^2}; \tag{1}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{2}$$

where R is the reflectance. By using both the transmittance and the reflectance, the absorption coefficient α was calculated. The extinction coefficient k was then calculated using α, and n was calculated using k and R.

Fig. 3(a) and (b) shows the variation of the refractive index n and the extinction coefficient k of the L-Ag NWs on glass, respectively, as a function of the wavelength in the interval from 300 to 1500 nm. We found that the extinction coefficient of the L-Ag NWs on glass was constantly close to zero over the wavelength range from 400 to 600 nm. The extinction coefficient of the L-Ag NWs/Glass dramatically decreased from 0.2 to 0.03 when the wavelength increased from 300 to 600 nm, slowly increased from 0.03 to 0.08 when the wavelength increased from 600 to 1300 nm. Moreover, the refractive index of the L-Ag NWs on glass was almost 2.2 over the wavelength range from 400 to 800 nm. The refractive index of the samples increased when the wavelength was larger than 800 nm. The values of refractive index n for the bare glass, being the difference about 0.2–0.4.

Khanarian [11] measured the refractive index of Ag NW thin films containing 20 and 30% w/w% of S-2/polymer film spin-coated on silicon wafers using a spectroscopic Woollam SE ellipsometer, and reported a maximum of the refractive index n of 1.54 at 450 nm, and a minimum n of 1.48 at 900 nm. However, in our study, we found that the average refractive index in the visible range of all the obtained films varied between 1.7 and 2.4. The refractive index of the Ag NW films depended primarily on the NWs density, length and diameter, as well as the measuring conditions.

We described the fundamental electron excitation spectrum of the film by means of a frequency-dependent function of the