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Full Length Article

Optical anisotropy studies of silver nanowire/polymer composite films with Mueller matrix ellipsometry

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ABSTRACT

Silver nanowire (AgNW)/photosensitive polymer composite film fabricated by roll-to-roll die coating exhibits optical and electrical anisotropy, depending on the coating conditions. To clarify the relation between the optical anisotropy, the electrical anisotropy and the orientation of AgNWs, the orthogonal optical constants of the composite films were determined by Mueller matrix spectroscopic ellipsometry. Multiple-sample analysis of reflection mode Mueller matrix and polarized transmission data was performed assuming a three-layer model consisting of substrate/polymer layer/conductive layer. The effective optical constants of the conductive layer revealed that the localized surface plasmon resonances, which arise from electric oscillation of along the short axis of AgNW, are large in the crosswise direction where the sheet resistance is large. On the other hand, the surface plasmon resonance associated with the electric oscillation along the long axis of the AgNW is large in the lengthwise direction where the sheet resistance is small. It seems the optical and electrical anisotropy reflects the morphology of the composite film, where the long axis of AgNW is preferably oriented in the direction lengthwise to the coated film.

1. Introduction

Silver nanowire (AgNW) networks are emerging as a next-generation transparent electrode material, given their high optical transparency and low electrical resistivity [1,2]. AgNW networks based transparent conductive film can be fabricated by cost effective wet coating methods [3,4] and exhibits better flexibility than the widely used indium tin oxide [5–7]. The optical and electrical properties of AgNW networks have been extensively investigated in the past decade, both experimentally [8–13] and theoretically [14–17]. For example, Colin Presto et al. reported that networks with smaller diameters of AgNW exhibit better performance than those with larger diameters due to higher optical transparency, even though higher AgNW concentrations enable low electrical resistivity [14]. Previous researchers have discussed some aspects of optical properties such as transparency and haze, but have not presented a comprehensive study concerning optical constants (refractive index n and extinction coefficient k) of the AgNWs network.

Recently, we have developed an AgNW/photosensitive polymer composite film that allows conductive patterning on a range of base materials. The composite films fabricated by roll-to-roll die coating exhibited optical and electrical anisotropy depending on the coating conditions such as shear velocity, convection and so on. These problems motivated us to study the relation between the optical anisotropy, the electrical anisotropy and the orientation of AgNWs in the polymer matrix.

In order to understand the optical properties, an accurate knowledge of the dielectric function or optical constant is of fundamental importance. Much research has been carried out on the dielectric function of the silver thin film [18–20], nanoparticle [21–25] and meshes with rectangular cross-section fabricated by the lithographic patterning [26–28]. Very few reports have focused on random AgNW networks fabricated by wet coating methods [9]. Although there have been a few investigations of optical anisotropy recently [29–31], there has been no report concerning the anisotropic optical constant of AgNW networks.

Here, we present the anisotropic optical constants of the AgNW/polymer composite films with spectroscopic ellipsometry. If a sample is partially depolarizing, extra care is required for ellipsometry analysis [32]. AgNWs networks cause depolarization due to the scattering of light. Mueller Matrix spectroscopic ellipsome-

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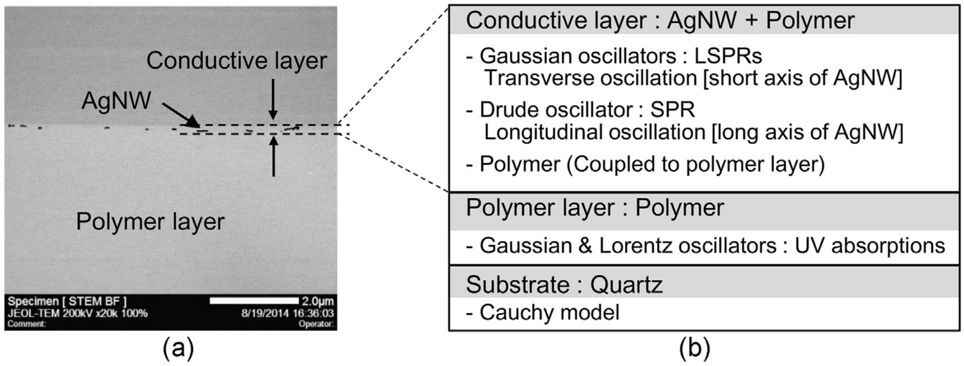

Fig 1. (a) Cross-section TEM image of the composite film, (b) Optical model applied in this ellipsometry analysis.

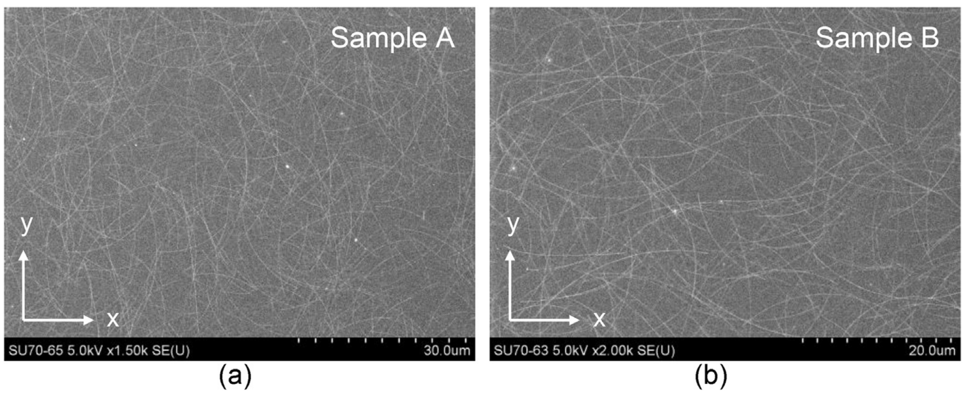

Fig. 2. SEM images of the composite film. Sample A shows a nearly random orientation of AgNWs while sample B exhibits a slightly restricting orientation of AgNWs. The x direction corresponds to the lengthwise direction and y corresponds to crosswise direction in roll-to-roll die coating.

try, which can handle both isotropic and anisotropic samples with and without depolarization, was used in determining the orthogonal optical constants.

Finally, we discuss the correlation between the optical anisotropy, the electrical anisotropy and the orientation of AgNWs in the polymer matrix.

2. Material and methods

The silver nanowires used in this study were obtained from a commercial source. The average diameter and length of the AgNWs are ca. 30 nm and 20 μm, respectively. AgNW/polymer composite films were fabricated using two-steps roll-to-roll die coating. First, the aqueous dispersion of AgNWs was coated on base film and dried. This was followed by the coating of a photosensitive acrylic polymer on top of the AgNWs. The polymer protects the AgNWs from environmental exposure and can be patterned on any substrates. Two samples with different degrees of orientation were prepared by controlling the coating conditions. Optical and electrical characterization were carried out using the samples, in which composite films were laminated to the substrate upside down, with AgNWs on top. The substrates used for all measurements were 1.0 mm thick quartz glass.

Angular dependence of the sheet resistances $R_s^{(\theta)}$ was calculated from the measured resistances $R_{measued}^{(\theta)}$ of narrow circuit lines arranged at 15° intervals. The sheet resistance of the circuit line directed at an angle θ, $R_s^{(\theta)}$ was calculated by $R_s^{(\theta)} = R_{measued}^{(\theta)} \times W/L$ where W and L were the width of 1.0 mm and the length of 30 mm, respectively. Patterned circuit lines were fabricated by photolithography.

Polarized absorption spectra as a function of the polarization angle were measured to support the ellipsometric analysis using an Agilent Cary 7000 Universal Measurement Spectrophotometer.

The effective optical constant and thickness of the composite films were determined using a dual rotating achromatic compensator spectroscopic ellipsometer (J. A. Woollam Co. RC2). The RC2 has dual rotating achromatic compensators both before and after the sample, and all 16 elements of the Mueller matrix (M11 to M44) can be collected with high accuracy.

The cross-sectional and in-plane images of the composite films were obtained with transmission electron microscopy (TEM) and scanning electron microscope (SEM), respectively.

3. Theory/calculation

Fig. 1(a) shows the cross-section TEM image of the composite film. The ellipsometry analysis was processed using a three-layer model consisting of substrate/polymer layer/conducting layer as shown in Fig. 1(b). Since AgNWs were embedded in the surface region of the polymer, we assumed a thin conductive layer consisting of AgNWs and polymer stacked on a thick polymer layer. Prior to the analysis of the conductive layer, optical constants of the substrate and the polymer layer were determined separately and fixed in the modeling. Polymer layer without AgNWs were prepared by chemically etching the surface of the composite film.

Quartz substrate is transparent over the visible region so the Cauchy dispersion model was used. The dielectric function of the polymer was described using multiple oscillators, Gaussian and Lorentz. Gaussian oscillators were chosen to represent the narrow absorption and a Lorentzian oscillator was added to account for broad absorption.