Robust thin spin-coated silver films with polymer thin layers for SPR image sensor applications

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ABSTRACT

We fabricated 20 nm-thick silver films with a 100 nm-thick low loss polymer on a prism using a spin coating method for surface plasmon resonance (SPR) image sensor module applications. The prism module was applied to an SPR image sensor system. The coefficients of determination for the 20 nm-thick silver films with and without the polymer layer were 0.9231 and 0.9228, respectively. The correlation is high-performed and the coefficients of determination are the same without reference to the polymer layer. The durability of the spin-coated silver film with the polymer layer is better than without the polymer layer. The spin coating method for the very thin silver and sequential polymer layers is expected to be a very cost-effective and robust solution because the layers are formed at a low temperature in a short period of time without requiring a vacuum system and the film has a much improved durability.

Keywords: surface plasmon resonance, image sensor, very thin silver film, spin coating method, transparent silver ink.

1 INTRODUCTION

Optical sensors based on excitation of surface plasmon, commonly referred to as surface plasmon resonance (SPR) sensors, measure changes in the refractive index occurring in the field of an electromagnetic wave supported by the optical structure of the sensors [1]. In general, sensitivity depends on the change of the refractive index of a dielectric as well as a variety of metals. SPR image sensor can monitor the change of the refractive index of dielectric molecules absorbing onto a metal surface with a relatively high degree of resolution [2]. Conventionally, all the thin metal films for SPR sensor module applications have been deposited by thermal evaporation or other vacuum deposition technologies. These vacuum deposition technologies are complex and requiring an expensive vacuum system and take a long time for deposition [3].

Nowadays, thin metal films are deposited and applicable to diverse components by using nano inks without requiring a vacuum system [4]. In general, below 100-nm-thick metal films on a prism are required for practical SPR sensor module applications. It is difficult to fabricate the thin films with thicknesses below 100nm by using a spin coating method with nano inks, where nano-sized metal particles are dispersed in a solution. Recently, the spin coating method with an ionic silver ink was introduced in order to fabricate very thin silver films with thicknesses below 100nm [5]. The developed spin-coated very thin silver films on the prism were applied and confirmed the possibility of SPR sensor module applications [6]. However, the durability of the module is very low. In this paper, the robust low loss polymer was introduced to overcome this weakness.

2 EXPERIMENTAL DETAILS

The transparent silver ink (trademarked TEC-CO-11) was supplied by InkTec Co., Ltd, Korea [7]. To control the thickness, the transparent silver ink solution was diluted with isopropyl alcohol. We used a surface adhesion promotor (trademarked ZAP-1010) that has amino-trimethoxy silane was synthesized and supplied by ChemOptics, Inc., Korea [8]. It is necessary to modify the prism substrate by using the surface adhesion promotor in order to form a silver film with good adhesion and high uniformity. The surface adhesion promotor solution was spin-coated on the prism and then baked at 110°C for 3 minutes on a hot plate for the hydrolysis process and the vaporization of the solvents present in the surface adhesion promotor. After the prism is treated by the surface adhesion promotor, the transparent silver ink was spin-coated on the prism and then thermally cured at 150°C for 10 minutes in a convection oven under a nitrogen atmosphere. To improve the adhesion between the silver and polymer layers, we used another surface adhesion promotor (trademarked ZAP-1020) that has methacrylate-trimethoxy silane was also synthesized and supplied by ChemOptics, Inc., Korea [8]. Again, the surface adhesion promotor solution was spin-coated on the prism and then baked at 110°C for 3 minutes on the hot plate. The UV-curable low loss polymer (trademarked ZPU450LV400) was supplied by ChemOptics, Inc., Korea [8]. Again, the UV-curable low loss polymer solution was spin-coated on the silver layer of the prism module.
Figure 1: Basic schematic view of the SPR sensor module.

the prism and then UV-cured in a UV oven for 5 minutes under a nitrogen atmosphere. The spin-coated silver film was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM).

We manufactured a home-made SPR imaging system, consisted of a 1 mW laser diode (LD) with telecentric optical lens and a TM polarizing filter, a digital CCD camera with telecentric optical lens, and the prism coated with silver. The light with the wavelength of 660 nm passes through the TM polarizing filter and impinges on the prism module with molecules at a specific angle of incidence. The reflected light is detected with the CCD and converted the intensity to an average gray value. We adjusted the angle to have the SPR angle with the darkest gray value when pure water was loaded in the SPR imaging apparatus in advance. The average gray value was defined as the average pixels value of a gray image which had values in the range of 0 to 255.

For SPR image sensor applications, we made the standard ethanol solutions with different ethanol contents. To make a 20.0% ethanol solution, ethanol and distilled water were mixed at a weight ratio of 2:8. Another ethanol solutions are mixed in the same way with different weight ratio. The range of ethanol solution is from 20.0% to 20.5% with 0.1% interval. The coefficient of determination ($R^2$) is calculated with the measured average gray values and the ethanol contents to assess how well ethanol contents are predicted with these prism modules.

3 RESULTS AND DISCUSSIONS

The prism module with the 20 nm-thick silver layer and the 100 nm-thick polymer layer for the SPR sensor are shown in Fig. 1. Figure 2 shows an SEM image of the 20-nm-thick spin-coated silver film with the surface adhesion promoter containing amino-trimethoxy silane. There were a lot of voids in the spin-coated solid silver film.

The thicknesses of the spin-coated silver film and the polymer layer were measured by AFM with the photolithographically etched steps. Figure 3 (a) and (b) show the AFM image and the measured thickness profile of the spin-coated silver film. The thicknesses of the spin-coated silver film and the polymer layer are 20 nm and 100 nm, respectively.

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The thicknesses of the spin-coated silver film and the polymer layer were measured by AFM with the photolithographically etched steps. The thicknesses of the spin-coated silver film and the polymer layer are 20 nm and 100 nm respectively. Even though the spin coating silver film was cured at the low temperature of 150°C for the short period of 10 minutes, the spin-coated solid silver film was well formed.
Figure 4 shows the results on feasibility test for the developed SPR image sensor modules of 20 nm-thick spin-coated silver film with and without the low loss polymer layer. For the SPR image sensor module of the 20nm-thick film without the low loss polymer, the coefficient of determination ($R^2$) is 0.9231, and for the SPR image sensor module of the 20nm-thick film with the low loss polymer layer, $R^2$ is 0.9228. The 100 nm-thick polymer layer on 20 nm-thick spin-coated silver film does not exert on the performance of the SPR image sensor because the $R^2$ values are same. The $R^2$ value of the SPR image sensor module without the polymer layer was deteriorated when it used once with the $R^2$ value of less than 0.9. However, The $R^2$ value of the module with the polymer layer was not deteriorated even when it used more than ten times with the $R^2$ value of more than 0.9.

The spin coating method for the very thin silver and sequential polymer layers is expected to be a very cost-effective and robust solution because the layers are formed at a low temperature in a short period of time without requiring a vacuum system and the film has a much improved durability.

4 CONCLUSIONS

We fabricated 20 nm-thick spin-coated silver films with and without 100 nm-thick low loss polymer on a prism for SPR image sensor module applications. The coefficients of determination for the 20 nm-thick silver films with and without the polymer layer were 0.9231 and 0.9228, respectively. The correlation is high-performed and the coefficients of determination are the same without reference to the polymer layer. The durability of the spin-coated silver film with the polymer layer is better than without the polymer layer.

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