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Surface Plasmon Resonance Sensor Using Grating Coupling Multimode Excitations

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1. Introduction

Surface plasmon resonance (SPR) spectroscopy has become a widely accepted method for the characterization and study of ultrathin films, interfaces and kinetic processes at surfaces, and been investigated in the applications of SPR sensors and plasmonic devices.[1-2] Many of them involved the enhancement of optical field due to the surface plasmon excitation at metal/dielectric intefaces. Among the surface plasmon excitation methods, one of the most well known techniques is a prism coupling method based on an attenuated total reflection configuration, while a grating coupling technique has not been widely used for the SPR sensing or plasmonic devices.[3-7] One major advantage of using the grating coupling excitation method is the fact that the prism is not necessary, hence inexpensive and disposable plastics can be used as the substrates, allowing for more flexible configurations.[8]

SPR sensors using white light source is a relatively new technique, which can provide multimode surface plasmon excitations in the multiple-wavelength region. Several approaches have been proposed to excite the multiple surface plasmons, including a selective beveling of the distal end of a fiber probe,[9] and a multi-pitch grating coupling technique.[10] In these studies, tuning the dynamic range and the improvement of the sensitivity have been reported, though the fabrication process was complicated.

In this work, we demonstrate a novel dopamine sensor using multimode surface plasmon excitations by irradiating white light source on metallic diffraction gratings /plastic substrates. Since the grating pitch is larger than commonly used diffraction gratings, multiple surface plasmon resonance excitations due to several diffraction orders were observed at same time. Layer-by-layer ultrathin films prepared from iron containing bis(terpyridine) polymer (Fe(II)-BTP) and poly(ethylene dioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS) were used as an electrochemical mediator for sensing the dopamine. Large changes in grating coupling surface plasmon dips were obtained upon an injection of the dopamine on the LbL/metallic grating surface.

2. Experimental

Recordable compact discs (CD-Rs: Mitsui Advanced Media Inc.) were used as diffraction grating substrates. First, CD-Rs were cut into several pieces, and then they were immersed into nitric acid in order to remove a dye layer deposited onto polycarbonate grating side. The cleaned polycarbonate grating substrates were covered with ca. 150 gold layer by vacuum evaporation. The grating samples were mounted on θ-2θ goniometer. A halogen lamp was used as the white light source for the excitation of surface plasmons. The p-polarized light was collimated by objectives, and was irradiated on the grating samples. The reflected light was detected by a photomultiplier after passing through a monochromator. The experimental configuration is schematically shown in Figure 1.

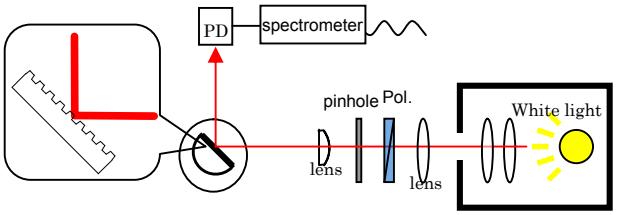

Figure 1. Experimental configuration of diffraction grating surface plasmon excitation

All potentiostatic and cyclic voltammetry measurements were carried out using a one compartment, three-electrode cell driven by an Hokuto Potentiostat (Model HZ-5000). In all the measurements, the working electrodes consisted of gold films (d ~ 47 nm) vacuum evaporated onto an S-LAH66 glass substrate (with an adhesion layer of 2nm Cr, previously evaporated on glass). The counter electrode was a Platinum wire and the reference an Ag/AgCl aqueous electrode. All the potentials reported in this paper are relative to this reference electrode.

Atomic force microscopy (AFM) experiments were done under ambient conditions with SPM-9600 (Shimadzu)

Figure 2 shows a strategy for the detection of dopamine using white light irradiation on grating substrate. In this sensing experiments, a conducting polymer, PEDOT, and bisterpyridine-Fe polymer were used as a mediator. Since these molecules change their dielectric constants in visible light region by oxidation/reduction, which depends on the doping state, it is expected that the SPR signals in

visible light region largely change upon an injection of dopamine because dopamine is oxidized with this film.

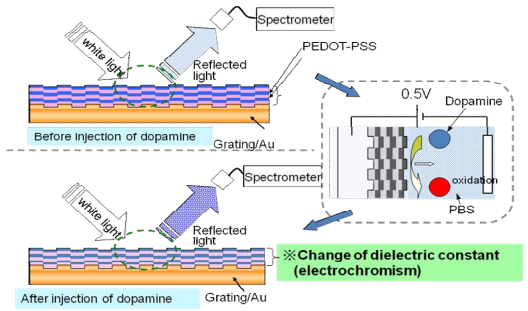

Figure 2. Strategy for the detection of dopamine

3. Results and Discussions

Figure 3(a) shows SPR reflectivity curves on the gold grating at fixed incident angles from 40° to 56° as a function of wavelength. As shown in this figure, many SPR excitation dips were observed in the measured region. The SPR dip of $+SP^{-1}$ mode shifts to lower wavelength as the incident angle becomes higher, while the dip moves to higher wavelength for $-SP^{+4}$ mode excitations. In order to analyze the data shown in Figure 3(a), the SP dispersion was plotted from each dip angle as shown in Figure 3(b). In this Figure, experimental SP dispersions obtained from each dip angle (dots) were plotted on the calculated surface plasmon dispersion branches (solid curves) at a silver grating/air interface. As shown in this figure, the plotted dots correspond to multiple diffraction modes, i.e. m = $+SP^{-1}$ and $-SP^{+4}$. As compared to commonly used grating pitches (ca. 400 to 800 nm), the grating pitch Λ used in this measurement (1.6μm) is much larger, therefore the distance between each excitation mode becomes smaller, allowing for the multiple SPR excitations in the measured region. As can be seen from the theoretical SP dispersion relations, 2 SP excitation conditions, i.e. $-SP^{+4}$ and $+SP^{-1}$, overlap with the wave vector of the incident light ranging from 800 nm to 400 nm at the incident angle of 40° and 56° (i.e. crossing points of red dashed lines and SP dispersion curves). The multiple SP excitations (circles) were indeed experimentally obtained as explained in the Figure 3(a), and corresponded with the theoretical SP dispersions as shown in this Figure. This result indicates that the multiple enhanced surface energies can be obtained on the grating which should be useful in the applications of photoelectric conversions, sensors and so forth. Furthermore, it should be noted that a large SPR dip was observed at 40°, which is at the crossing point of m=-1 mode and +4 mode, indicating the superimposed SP excitation of 2 modes can be obtained. This large dip was again split to m=-1 and +4 modes, respectively at 42°.

3. Conclusions

In summary, grating coupling multiple surface plasmon excitations were studied upon an irradiation of white light on CD-R metallic diffraction grating /plastic substrates. As the grating pitch was large enough, multimode surface plasmon excitations could be obtained. The SPR dips were sensitively shifted when layer-by-layer ultrathin films were deposited on gold grating substrates. The experimentally obtained SP dispersion was corresponded well with theoretical SPR dispersion curves. Further investigation of dopamine sensing properties are underway.

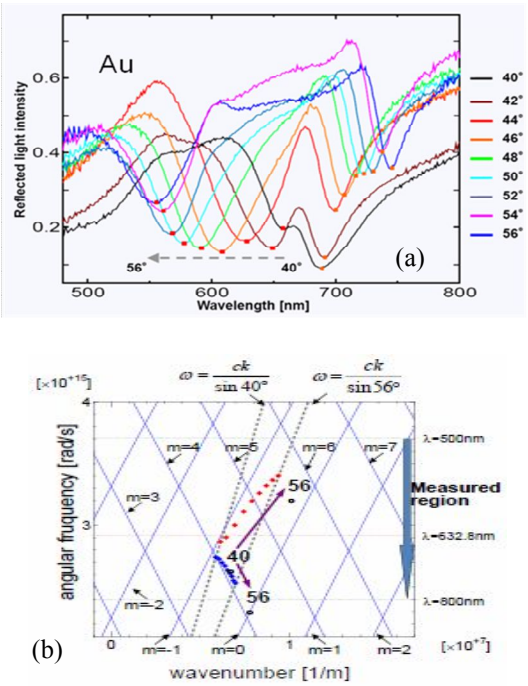

Figure 3 (a) SPR reflection curves on a gold grating at fixed incident angles from 40° to 56° as a function of wavelength. (b) Plotted dots obtained from experimental dip angles and calculated SP dispersion branches.

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