Deep-ultraviolet light excites surface plasmon for the enhancement of photoelectron emission

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(Received 19 October 2010; accepted 2 December 2010; published online 20 January 2011)

We show deep ultraviolet (DUV) light excitation of surface plasmon resonance (SPR) (DUV-SPR) with aluminum (Al) film. DUV-SPR has higher energy than that of visible light opens many applications, such as enhancement of photoelectron emission from metal surface, autofluorescence imaging of biological specimens, and laser ablation with high energy photons. We demonstrated the enhancement of photoelectron emission by DUV-SPR and analyzed protection layer to avoid oxidation of aluminum surface with enhancement of electric field kept as much as possible. The photoelectron emission from the aluminum surface was enhanced nine times with the excitation of SPR. © *2011 American Institute of Physics*. [doi:10.1063/1.3537823]

I. INTRODUCTION

Recently, many researchers have studied on surface plasmon resonance (SPR) and applied it to various fields, such as spectroscopy, biosensing, material analysis, near-field optics. SPR has advantages of electric field enhancement, high sensitivity to refractive index change in materials near the metal surface, electric field localization near the surface of the metal film. These advantages are applied for surface-enhanced Raman scattering (SERS),[1] measurement of refractive index and thickness of monolayer film[2,3] apertureless scanning near-filed optical microscopy with local SPR,[4,5] detection of immunoassay reactions, etc. In many studies and applications red or near-infrared lights were used for excitation of SPR, because silver and gold are good materials for excitation of SPR in these wavelength region.

Aluminum is a best plasmonic material in deep ultraviolet (DUV) region. Since light frequency in DUV region are larger than the plasma frequencies of the metals such as silver (Ag) and gold (Au), the light propagates inside the metals and is much absorbed. These metals are not suitable materials for the excitation of SPR in DUV region. Localized surface plasmon resonance in nanoparticles, nanorods[6] and nanodisks,[7] SPR,[8] and extraordinary optical transmission through hole arrays[9] in UV or DUV region have been studied. DUV plasmon are applied for SERS,[10] tip-enhanced Raman scattering,[11] fluorescence enhancement.[12,13] Analysis of biological sample in DUV region has advantages because an electronic resonance enhancement was shown on nucleic acids, amino acids, and proteins. DUV plasmon is capable of label-free detection and imaging of biomolecules.

We present DUV light excitation of SPR (DUV-SPR) with aluminum (Al) film. DUV light has higher energy than that of visible light, so DUV-SPR opens many applications, such as enhancement of photoelectron emission from metal surface, fluorescent observation of biological specimens without labeling dyes, and laser ablation with high energy photons. In this paper, we demonstrated the enhancement of photoelectron emission from metal surface.

Tsang *et al.*[14] demonstrated the enhancement of photoelectron emission from metals of Ag, Au, and Al by using multiphoton process. They used near-infrared light and multiphoton process for the excitation of photoelectrons. We used UV light of 224.3 nm wavelength that has enough energy to emit photoelectron from metals, such as Au, Ag, and Al.

The value of plasma frequency for Au and Ag which are well-known metals for SPR are 1.37×10^{16} and 1.36×10^{16}, respectively.[15,16] For Al, the value of plasma frequency $\omega_p = 2.4\times10^{16}$, which is in the ultraviolet, is higher than those of the other metals. Plasma frequency of Al is larger than the others, so real part of Al dielectric constant larger in DUV region. Imaginary parts of other dielectric constant of Ag, Au, and Cu increase in DUV region due to the interband transition. However, Al does not have an interband transition in DUV region, so imaginary part of Al complex dielectric constant is small in DUV region. Since Al has a large real part and small imaginary part of dielectric constant in DUV region. Al is good material for SPR excitation in DUV region.

We calculated the reflectance of four layers model using Fresnel's transmission and reflection coefficients.[17] The calculations were taken into account for effect of oxidization of Al, because Al is easy to be oxidized in air.

Figure 1 shows the calculation model of four layers that is consisted of SiO_2, Al, and the vacuum. The refractive index at 224.3 nm wavelength of SiO_2, Al, Al_2O_3, and vacuum are 1.52, 0.16+2.62i, 1.85+0i, and 1.00, respectively.

Figure 2(a) shows calculation results of reflectance dependence on the incident angle and thickness of Al film without oxidation. The thicknesses of Al film were 17, 19, 21, 23, and 25 nm. It was found that SPR was occurred at around 45° for every Al film thickness and the thickness in which the reflectance becomes lowest was 21 nm in enlarged view

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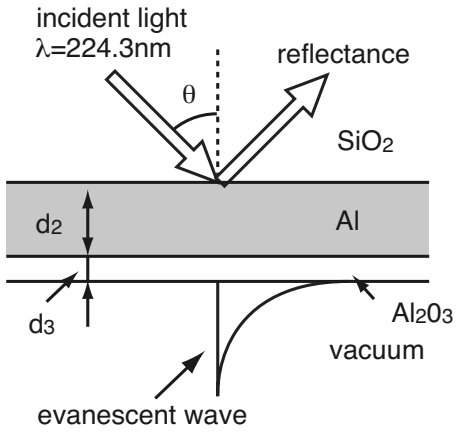

FIG. 1. Schematic diagram of calculation model of four layers. The layers are consisted of SiO_2, Al, Al_2O_3, and the vacuum.

of Fig. 2(a). We decided the thickness of Al film is 21.3 nm from detail calculations. Figure 2(b) shows calculation results of reflectance dependence on the incident angle and thickness of oxidation layer. Thickness of Al film was d_2 =21.3 nm. Thickness of the oxidation layer d_3 was varied from 0 to 10 nm. It was found that as thickness of the oxidation layer increases, the excitation angle is shift to larger angle and the adsorption dips become shallower and wider.

II. EXPERIMENTAL SETUP

Figure 3 shows an experimental setup to measure the photoelectric current and reflectance of light. Al film was

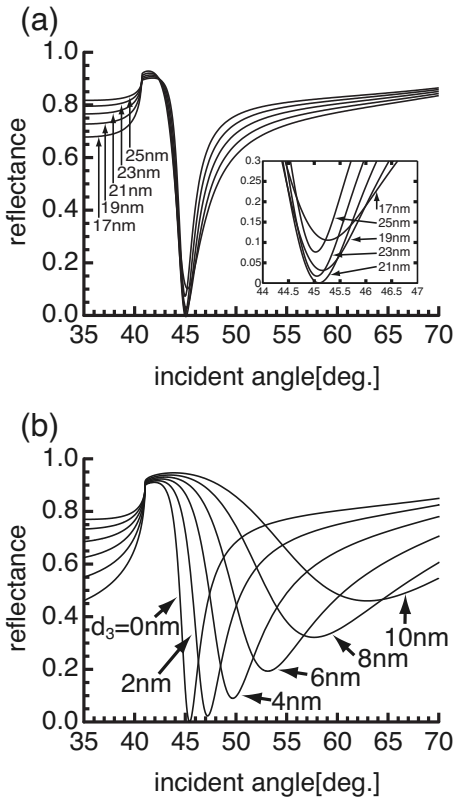

FIG. 2. Calculation results of reflectance. (a) Changes in the incident angle and thickness of Al film without oxidation. (b) Changes in thickness of oxidation layer. The thickness of Al film was 21.3 nm.

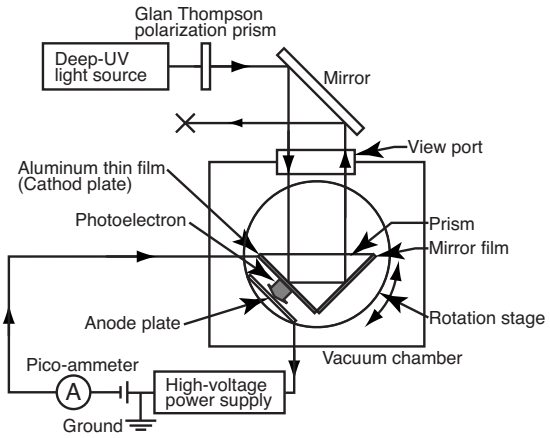

FIG. 3. Experimental setup to measure the photoelectric current enhancement by SPR. Deep-UV light source, He–Ag laser, wavelength 224.3 nm, frequency 1 Hz, 0.1 ms pulse width; accelerating voltage, anode −20 V, cathode 1 kV, and distance between anode and cathode 1 mm; picoammeter, sampling frequency 28 Hz, integral time 16.6 ms, and resolution 10 fA.

evaporated on quartz glass prism in vacuum with the thickness of 21.3 nm. The prism with thin Al film is placed on a rotation stage in the vacuum chamber ($\sim 10^{-4}$ Pa). DUV light is incident to the prism through a view port made of quartz. The emitted photoelectrons from Al thin film are detected with the anode plate by applying high voltage. We measured the current of the cathode with a picoammeter. The dependence of photoelectron current on the incident angle of light to the Al film was measured. The reflectance of light at the Al film was also detected at the same time. We measured the photoelectric current with *p*-polarized and *s*-polarized light.

Figure 4(a) shows experimental results of dependence of photoelectric current on incident angle with *p*- and *s*-polarized lights. Because of the limitation of optical setup the incident angle was divided in following three parts: 40°–48°, 44°–54°, and 50°–60°, in order to get the dependency in a wide range. The measured photoelectric currents of the same incident angles in different parts were different slightly,

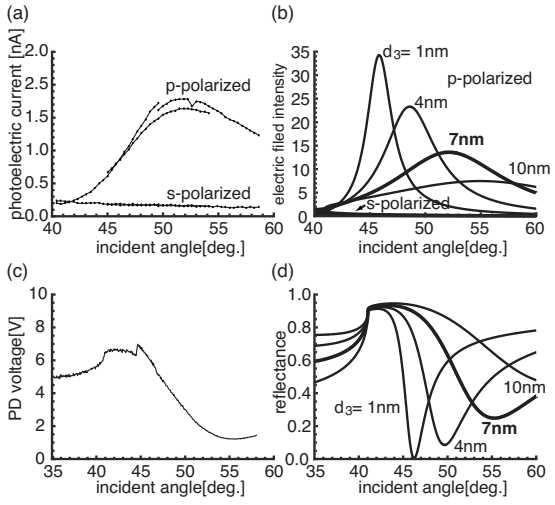

FIG. 4. Experimental and simulation results of photoelectric current enhancement by SPR and reflectance. (a) Experimental results of photoelectric current. (b) Calculations of electric filed intensity. (c) Experimental results of reflectance. (d) Calculations of reflectance.

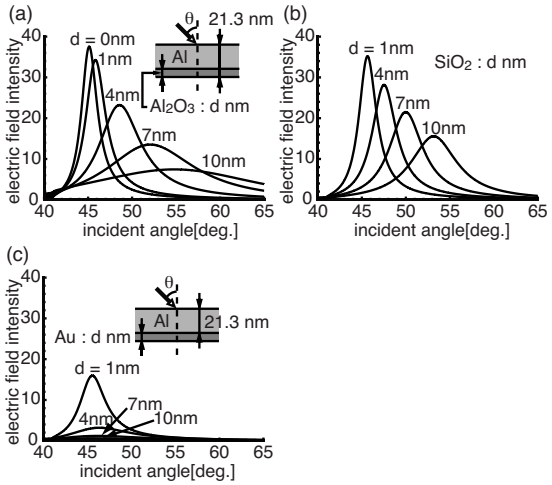

FIG. 5. Dependence of enhancement ratio on the thickness oxidizing Al film surface. (a) Al_2O_3 model. (b) SiO_2 cover model. (c) Au cover model.

because the gap distance between the prism surface and the anode plate was not exactly same for each measurement. The photoelectric current depends on the gap distance. In our system, it was difficult to set the prism at exactly same position for each measurement. In the case of *p*-polarization incident, photoelectric current was enhanced in the range of angle 45°–60° and had the peak at 52°. Photoelectric current is enhanced nine times at the maximum value. On the contrary in *s*-polarization incident, the photocurrent was constant and low in entire incident angle range.

Figure 4(b) shows the calculation results of electric field intensity to incident angle of light with various thickness of oxidized Al film. The intensity was normalized with the value of incident light intensity at 40°. Compared with calculations and experimental results, the simulation result of 7 nm Al thickness well agrees the experimental result.

Figures 4(c) and 4(d) show experimental and simulation results of reflectance with *p*-polarized light, respectively. The reflectance of experimental result was normalized with the reflectance with the minimum value. We calculated reflectance with four different thicknesses of oxidized Al films. The peak of reflectance at the angle 45.4° was caused by the reflection at the boundary between the prism and the vacuum in Fig. 4(b). Compared with experimental results and calculations, these curves decrease at the same angle and the results show good agreement with calculations that thickness of aluminum was oxidized with 7 nm thickness.

As a result of it, we may conclude that SPR was excited with DUV *p*-polarized light and enhanced emission of photoelectrons. We discuss on coating a protection layer to avoid oxidization of Al film. If there is no oxidization on Al film surface, we can expect 40 times enhancement factor with 21.3 nm thickness film for the light of 224.3 nm wavelength. In the case of oxidization with 7 nm, the enhancement factor decreases to about ten times.

Figure 5(a) shows the dependence of enhancement ratio on the thickness oxidizing Al film surface. We calculated the models in which SiO_2 and Au were coated on Al film as a protection layer. Although the field enhancement factor is decreases with increasing thicknesses of SiO_2 and Au layers, the enhancement factor in SiO_2 coating is lager than that of oxidized Al film. By using SiO_2 of 7 nm thickness, the enhancement factor is expected to increases 1.5 times. While in Au layer the enhancement factor is low in every layer thickness because Au has large imaginary part of dielectric constant in DUV region. The refractive index of gold at 224.3 nm wavelength is 0.38+4.17i. Therefore, Au layer attenuates plasmon oscillation strongly. As a result of it, thicker Au layer much decreases the SPR electric field intensity, as shown in Fig. 5(c). In SiO_2 layer case, the absorption is negligible, but the protection layer gives mismatch from SPR condition. Consequently, decrease in the enhancement ratio with increasing SiO_2 protection layer was smaller than that in Au layer case.

III. CONCLUSIONS

We demonstrated that the enhancement of photoelectron emission by exciting SPR in DUV region. We founded that Al is good material to excite SPR in DUV light. Experimental results of reflectance and photoelectric current show good agreement with theoretical calculations, if we assumed Al film was oxidized with 7 nm thickness. The photoelectric current was enhanced nine times due to field enhancement by SPR. We discussed the protection layer to avoid oxidization of Al film. We also confirmed that 193 and 248 nm wavelength light could excite SPR with Al film and could expect enhancement factor as large as the case of 224.3 nm wavelength. We believe that DUV-SPR opens new applications in various fields.

ACKNOWLEDGMENTS

This work has been supported by CREST of JST (Japan Science and Technology Agency).

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