Optical Characterization of the Au Nanoparticle Monolayer on Silicon Wafer

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ABSTRACT

This paper mainly studies the optical property of gold nanoparticle films and its variations under different surface coverages. Au nanoparticle monolayers with different surface densities are prepared and its optical constants are decided by variable-angle ellipsometry at 530nm and 643nm, respectively. The extinction coefficient shows a linear correlation with the surface coverage, nonetheless the refractive index n presents a more complex behavior. This measured optical constants are compared to the theoretical estimations of effective medium theory(EMT); both Maxwell-Garnett and Bruggeman models are employed. Neither of these two theoretical predictions fit in with the experimental results. When the surface coverage is nearly full, the optical constant does not approaches to the bulk values as predicted by EMT, which implies the Au nanoparticle film has distinct optical property from the bulk gold and calls for a deeper understanding in its electronic structure.

Keywords: effective medium, nanoparticle, film, refractive index

1 INTRODUCTION

In recent years, self-assembly technique has been widely used in fabricating mono- or multi-layers of Au nanoparticle layer for various applications. The nanoparticle layer is covalently linked with a linker layer on the substrate, so its structure is more stable and the spacing can be controlled by the length of linkers. It has been shown that Au nanoparticle layer made this way has promising applications in biosensor, since the optical absorption of this layer is very sensitive to the optical properties of ambient medium . The optical characterization of this layer and understanding how it changes with ambient environment are crucial in elucidating the sensing mechanism and developing better devices. However, up to now there have been very few reports on the optical constant, N=(n+ik), of the covalently -linked nanoparticle monolayer[1]. .

Before performing the measurement of optical constant for this nanoparticle film, there is another factor needed to be considered. Different from typical gold film, Au nanoparticle film is discontinuous so has a lot of boundaries, which are in contact with the ambient medium. What we measure as the optical property is actually due to the nanoscale mixing effects of Au nanoparticles and the medium. That may be the reason why the optical absorption is so sensitive to the medium. Different surface mixing conditions give rise to different values for optical constant. For the optical constant to be unambiguously referred, the mixing factors, such as surface density, the shape and size of the grain, need to be specified. So here surface coverage (or density) is chosen as a mixing factor, the optical constant is studied in terms of the surface coverage.

In this study, the surface coverage is decided by counting the covering area in AFM images. When the coverage is nearly full, the optical constant is not approaching that of bulk gold, as we supposed beforehand. The measured values are also compared with the results estimated by two effective medium theories, Maxwell-Garnett and Bruggeman models. Both fail to predict the experimental data. It suggests the nanoparticle film has distinct optical properties which cannot simply approximated by linearly adding and averaging two bulk materials, as it is done in classical effective medium models.

2 METHOD

In this section, the experimental methods will be described. It includes three parts: i) the chemical preparation of Au nanoparticle film with different surface coverages, ii) the ellipsometric measurement to obtain the optical constant n and k, iii) the AFM measurement of the the height and the surface coverage.

2.1 Preparation of Au nanoparticle film

Derivatization of silicon wafer Polished silicon wafer is used as the substrate for its flatness and suitability for ellipsometry. It is first cleaned in piranha solution at 60°C (H2SO4/H2O2) for 30min, and is then derivatized by immobilizing APTMs (3-Amino-propyl-trimethoxysilane)

on it. APTMs is purchased from Sigma and then further diluted to 1.1mM in ethanol. The derivation of silicon wafer is made by immersing the wafer in 1.1mM APTMs for 3hrs. After it, the substrate is thoroughly washed by ethanol and H2O. It is stored in H2O before use.

Immobilization of Au nanoparticles Colloid Au (20nm) is purchased from Sigma. The undiluted solution has a absorbance value 1.67 at 531nm. The different coverages of nanoparticle film are made possible by immersing silicon substrate in different concentrations of colloidal Au. The Au colloidal solution is first diluted as 1/2,1/3,1/4,1/5 of original concentration. Five silicon substrate is prepared. The substrates are first dried by nitrogen and then are immersed 1,1/2,1/3,1/4,1/5 diluted colloidal Au solution and sit for six hrs. The samples are then washed by H2O and dried by nitrogen for further investigation.

2.2 Ellipsomeric measurement

A variable-angle ellipsometer made by Nanofilm, Germany is used to study the optical properties of the nanoparticle film. The light source is 530nm and 643nm laser. For each sample , ellipsometric measurement is performed at various angle of incidence from 42 °to 62 ,°at 5 °intervals. Taking the measured height 17.5nm in AFM as the thickness, n(refractive index) and k(extinction coefficient) are obtained by employing the 3-layer Fresnel equation to fit the ellipsometric parameters Delta and Psi. Very good fit (MSE 10e-1) are obtained, which indicates the validity of the fitted n and k. For each sample, the measuring area is around 1*1mm; three positions are chosen for measurement and the average n,k and standard deviation of are calculated.

2.3 Surface coverage measurement

DME(Danish Micro Engineering) atomic force microscope is used to measure the surface topology of the nanoparticles film. Tapping-mode is adopted in whole scanning. The images are taken in 2*2um and 1*1um regions. The height is obtained by averaging the difference of 5 highs and lows in each profile. The 17.5±0.6nm is the average of 20 profiles taken from 5 images. The surface coverage of each image is decided by counting the pixel which value is above set threshold; the number of these pixels divided by total pixels is the surface coverage.

3 RESULTS AND DISCUSSION

Different coverages are attained by immersing substrate in different concentrations of colloidal gold as expected. The different coverages are observed by AFM; the images (2*2um) are shown as in the figure 1. (a) 97% (b) 72.2% (c) 58.1% (d) 49.8% (e) 9% (g) line profile of (b) figure

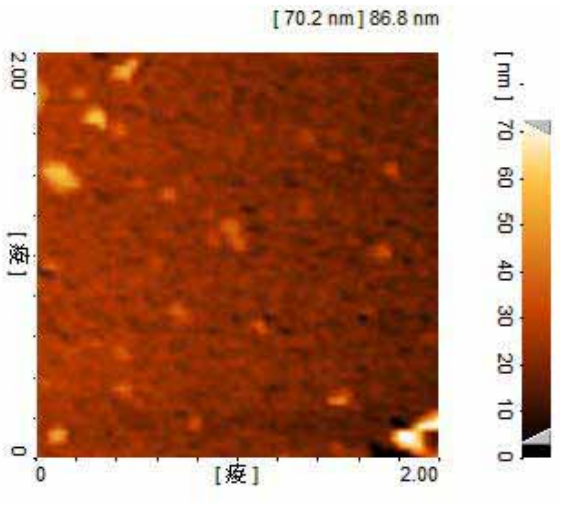

Fig 1.(a) Immersion in undiluted colloidal gold makes the 97% surface coverage

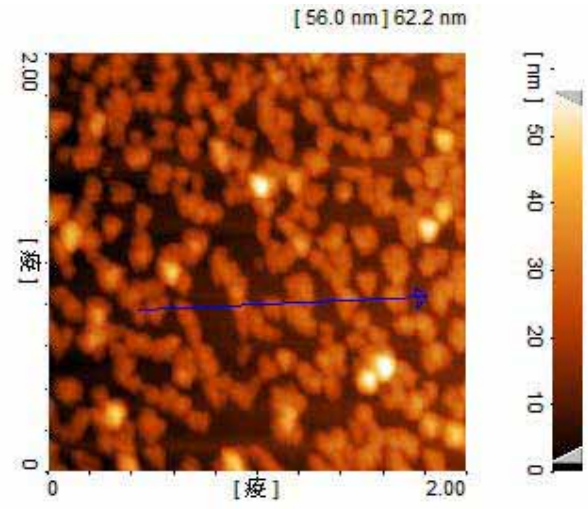

Fig.1.(b) Immersion in 1/2 diluted colloidal gold makes 72.2% coverage. A line is drawn to show the profile. See fig.1(g)

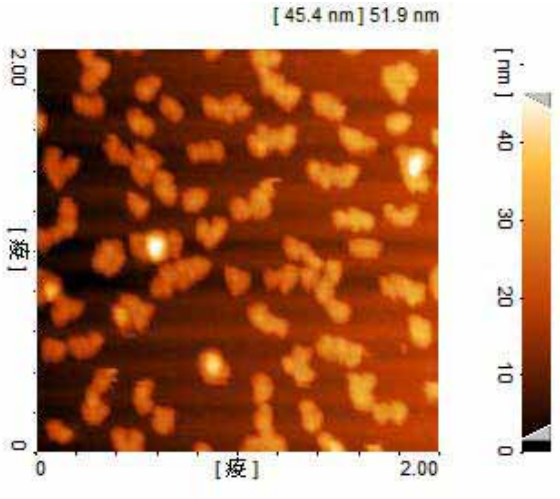

Fig.1(c) Immersion in 1/3 diluted colloidal gold makes 58.1% coverage

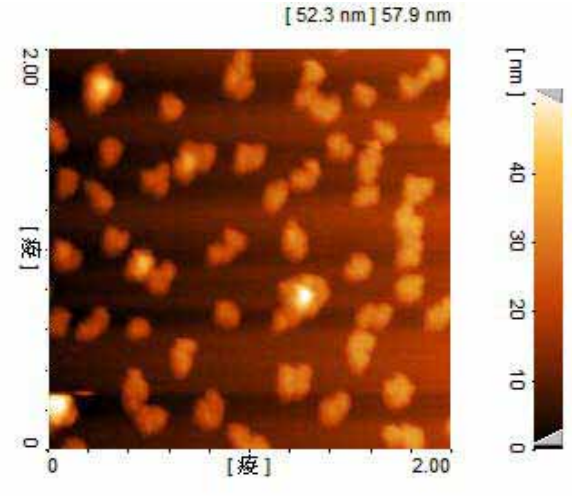

Fig.1(d) Immersion in 1/4 diluted colloidal gold makes 49.8% coverage

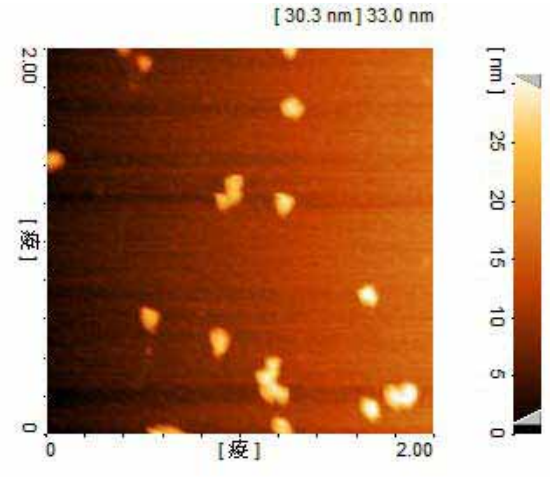

Fig.1(e) Immersion in 1/5 diluted colloidal gold makes 9%coverage

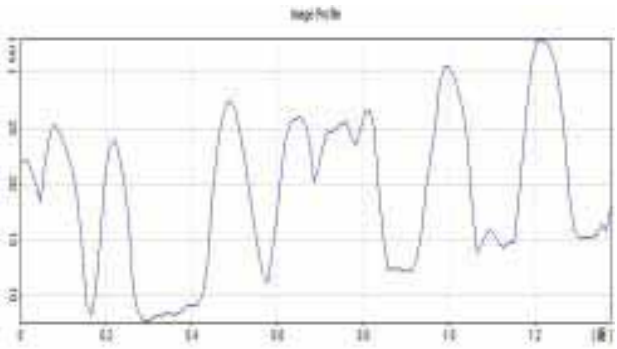

Fig.1(f) Line profile of Fig.1(b)

The measured n and k varies with surface coverage as expected. The extinction coefficient k shows an approximately linear relation with the surface coverage. The relation of k value vs. surface coverage at 530nm and 643nm is shown below in Fig.2. The correlation coefficient r is 0.96, indicating the high correlation between these two variables: k and surface coverage. Though large numbers of data are required to test to see if the relation is truly linear, and statistical work is needed for putting such an application into practice, this simple result at least sheds a little light on the future direction.

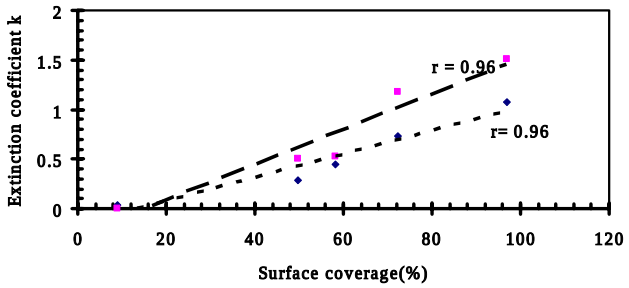

Fig.2 **Square**: k values at 643nm **Diamond:** k values at 530nm

However, the refractive index does not exhibit a simple monotonously increasing or decreasing relation(See Fig.3).

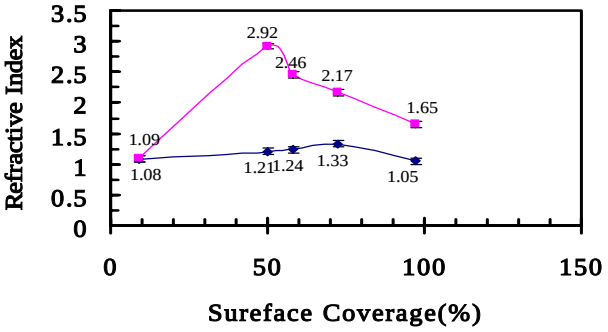

Fig.3 **Square**: n values at 643nm. **Triangle**: n values at 530nm

The error bar indicates the variation between different points on the same sample; for each sample, 3 different points are measured. Only slight changes of Delta(< $\pm$0.5) and Psi(< $\pm$0.1) are observed, so the variation of millimeter –average n,k is small as ±0.05.Effective medium models are employed in hopes of explaining the complex behavior. The value of surface coverage is substituted for the volume fraction f in Maxwell-Garnett and Bruggeman models to decide the effective n and k of this discontinuous film. Equation 1 is the expression of Maxwell-Garnett formula in this example(choosing Au as host material and air as the ambient).

$$\frac{\varepsilon_{eff}-\varepsilon_{au}}{\varepsilon_{eff}+2\varepsilon_{au}}=(1-f)\frac{\varepsilon_{air}-\varepsilon_{au}}{\varepsilon_{air}+2\varepsilon_{au}} \quad (1)$$

Equation 2 is Bruggeman formula;

$$f\frac{\varepsilon_{au}-\varepsilon_{eff}}{\varepsilon_{au}+2\varepsilon_{eff}}+(1-f)\frac{\varepsilon_{air}-\varepsilon_{eff}}{\varepsilon_{air}+2\varepsilon_{eff}}=0 \quad (2)$$

ε_{eff} is decided accordingly and the corresponding n and k ($\varepsilon=(n+ik)^2$) is then calculated. The results are shown in Fig.4

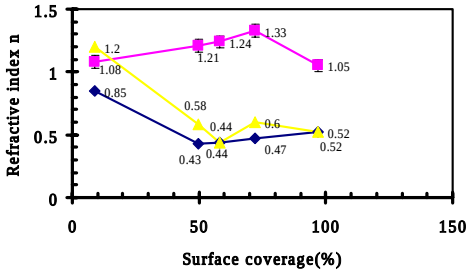

Fig.4 **Square:** n values measured at 530nm **Triangle:** Bruggeman's prediction **Diamond:** MG's prediction

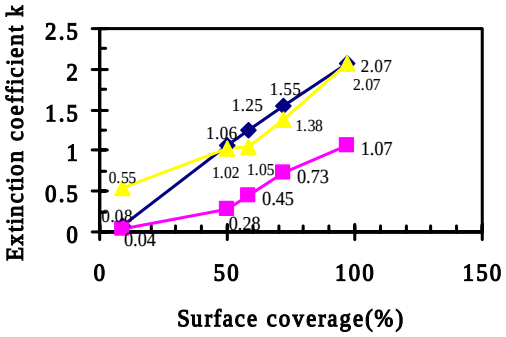

Fig.5 **Square**: k values measured at 530nm **Diamond:** MG's prediction **Triangle:** Bruggeman's prediction

Both MG and Bruggeman models predict an increasing k with the surface coverage(See Fig.5). But for the part of n, MG and Bruggeman models neither successfully describe its relation with surface coverage nor give prediction close to the measured values. As to the optical constant when the coverage is full, both MG and Bruggeman models give the bulk result; ie, n and k are 0.52 and 2.13; this disagrees with the measured n and k values ,1.05 and 1.07. it is very different from that of bulk gold, which has the value as 0.52 and 2.13. It is supposed that with the presence of boundaries at nanoscale, the electrons in the nanopaticle film are no longer in an infinite crystal potential field, as they are in bulk gold. The electronic band structure has become different with the existence of a different potential field. This difference then gives rise to the distinct optical properties as observed in experiments. This thinking also implies that the mixing factors, including grain size and shape ,density, and topology, etc, may play important roles in the optical properties.

4. CONCLUSION

From the data above, the extinction coefficient appears to be a candidate for quantifying the surface density, which surely is a measure of surface amount as long as the distribution is random. As to the n, k values of the Au nanoparticle film, the measurement does not agree with the theoretical approximation, which prediction approaches to the bulk gold when the surface coverage gets saturated. But experiment shows that Au nanoparticle film has n,k very different from that of bulk gold. It seems to imply that this Au nanoparticle film, composed of grains at nanoscale, has different electronic structure from bulk gold, and its optical effects cannot be reduced to the linear addition of the effects of two bulk material, gold and air.

REFERENCES

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