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FREQUENCY RESPONSES OF Au NANOPARTICLES IN POLYURETHANE RESIN

Chen Hsu and Yi-Chi Liou

Department of Mechanical Engineering, Chung Cheng Institute of Technology, National Defense University, Da-Hsi, Tao-Yuan, Taiwan 335, Republic of China

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Abstract. The frequency properties of Au nanoparticles in polyurethane have been investigated. The Au nanoparticles prepared by phase transfer method were added to polyurethane resin and hardened with polyisocyanate. The permittivity, permeability, and frequency reflective loss of the resultant nanocomposites were measured and calculated. From the experimental results, the frequency responses of the hydride resin have demonstrated to be affected with the little addition of Au nanoparticles. The electric permittivities and magnetic permeabilities of Au-nanoparticle-imbedded resin arise from the cut-off frequencies of about $9.0 \cdot 10^8$ Hz. However, the magnitudes of those permitivities are not proportional to the amount of Au nanoparticles in the resin. The fluctuation of frequency response might come from the coupling effect from the polarization of nanoparticles under electromagnetic field and shield their own on the high concentration of addition. As a result, the reflective energy loss takes place with the addition of Au nanoparticles.

1. INTRODUCTION

The existence of metal nanoparticles in matrix has demonstrated to affect the properties of heterostructures. For example, the electron transfer is observed in the self-assembled inorganic polyelectrolyte/meal nanoparticle heterostuctures [1]. The optical properties of metal nanoparticles not only depend on the band structures of metal nanoparticles but also on the dielectric behavior of host matrix. The substrate can enhance the coupling of the Au nanoparticles [2,3]. Metal nanoparticle arrays show the surface plasmon coming from the interparticle coupling [4-6]. However, the role of the metal nanoparticles themselves on the frequency response is not intensively investigated. In this study, Au nanoparticles are intentionally added to the polyurethane resin, which is not sensitive to the electromagnetic wave, for revealing the roles of metal nanoparticles on the frequency.

The frequency properties of metal nanoparticles in the substrates depended on the dielectric function of metal nanoparticle, and have been evaluated by classical Drude theory, quantum simulation, and a DFT-based approach [7,8]. The absorbing property is characterized by large values for the imaginary part of the permittivity and permeability. The ratio of the imaginary to the real parts of these electromagnetic parameters is related to the tangent loss. The mean absorption cross section of a single particle of volume V is given by the following Mie equation [9].

Corresponding author: Chen Hsu, e-mail: hsen@ccit.edu.tw

$$\kappa = \frac{9V\omega\varepsilon_m^{2/3}}{c} \frac{\varepsilon_2(\omega)}{\left[\varepsilon_1(\omega) + 2\varepsilon_m\right]^2 + \varepsilon_2(\omega)^2}, \quad (1)$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are real and imaginary parts of the (isotropic) dielectric function of the particle, ω the optical frequency, ε_m the dielectric constant of the host medium, assumed independent of the frequency. According to the Drude model, the real and imaginary parts of the dielectric function are affected by the angular frequency, the bulk plasma frequency and the damping frequency. By the quantum box model, the dielectric function can be determined by the angular frequency and the Fermi-Dirac occupation factors. Density Functional Theory (DFT)-based quantum chemistry constitutes the most largely employed ab initio approach for the study of the electronic behavior of metal clusters. The frequency response, therefore, becomes an important parameter on the determination of related properties.

2. EXPERIMENTAL PROCEDURES

Various amounts of Au nanoparticle solutions were prepared by phase transfer method [10] and mixed with polyurethane resin for further frequency tests. The transferred nanoparticles were then capped with surfactants in solution to inhibit the growth of nanoparticles. To prepare Au nanoparticle, 2 ml of 0.01M $HAuCl_4$ aqueous solution were mixed and stirred with 0.18 g of 10 ml cetyl-trimethyl ammonium bromide C16TAB aqueous solution. After 5 minute, 5 ml of deionized aqueous solution with 0.02 g $NaBH_4$ was added at a rate of one drop per second, and then stirred for one hour. After the decomposition of the aqueous solution with toluene, the nanoparticles were formed in the toluene part.

1~10 ml of the solutions were added in 100 ml of polyurethane resin, which was diluted with 25 ml of xylene and hardened by 10 ml of polyisocyanate. Transmission electron microscope was used to observe the morphologies of the Au nanoparticles. The prepared solution was dropped on carbon film which was deposited on Cu grids and waited for 30 seconds. The extra water was absorbed by filter papers. The samples were observed using a Philips CM200 high resolution electron microscope (HRTEM). The structures were analyzed by selected area diffraction technique (SAD). The chemical compositions were analyzed by X-ray energy dispersive analyzer (EDAX) which is equipped on HRTEM.

UV/VIS spectrum were carried out to measure the absorption of visible light (380~780 nm) and ultraviolet light (200~380 nm). The absorption of UV could use to analyze inorganic and organic materials. Because the valence electron can be activated by UV, for gas atom or simple molecule, the absorption spectrum present a series of sharp lines which is corresponding to transition of electron. For molecules or ion in solution, the energy difference of vibration or rotation from each electron state causes the absorption line closely arranged as smooth, continuous, and wide band of absorption band. The UV light source used was Deuterium lamp. The visible light source was tungsten lamp. The measurable absorption wave range is between 175-3300 nm, and the resolution is 0.05 nm. The quartz container was used to set the solution. Comparing with bulk materials, the absorption band for nanoparticles have blue shift phenomenon due to the quantum and surface effect.

The frequency behaviors for the Au nanoparticles imbedded in painting were measured using a Hewlett Packard HP4291B RF impedance analyzer from 1MHz to 1.8GHz at room temperature. The dielectric permittivity and magnetic permittivity of Au-imbedded paint were measured and then the reflective loss was calculated. The real part of dielectric permittivity indicates the energy could be stored under external electrical field. The image part is related to the loss of energy in the external electrical field.

3. RESULTS AND DISCUSSION

Fig. 1 shows the transmission electron microscopy image of Au nanoparticles prepared by phase transfer method. Most of the particle size of nanoparticles fells into the range of 5-10 nm, and various morphologies are presented. The Au nanoparticles enclosed with various facets are related to the growth rate, R, in <100> to that of the <111> during the preparation processes. The main morphologies consists of truncated octahedral (TO), twined TO, and iscosahedral (Ih). The TO particles were grown with the ratio between 0.87 and 1.73 and enclosed with the {100} and {111} facets. The Ih of multiple twinned particles (MTP) is also exhibited. The twining could arise from the release of the stored energy during growth and take place on the (111) plane.

Fig. 2 shows a typical absorption spectrum for Au nanoparticles. The maximum of the SPR absorption position is located on the mean of 520 nm for Au nanoparticles. This peak position corresponds to the surface plasmon resonance of Au nanoparticles. This demonstrates that the prepared solutions own the existence of Au nanoparticles. The prepared solutions with Au nanoparticles were added to polyurethane resin with various additions

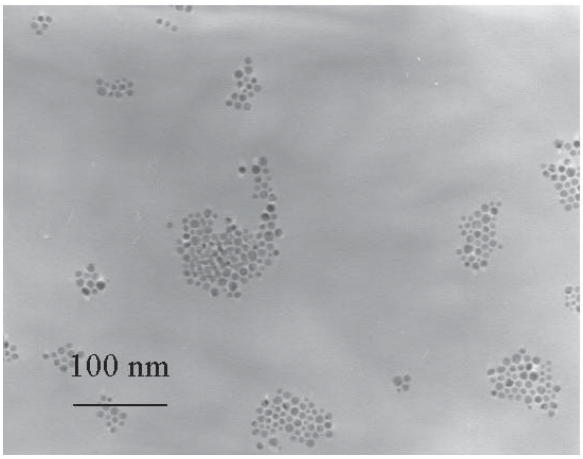

Fig. 1. Transmission electron microscopy image of Au nanoparticles.

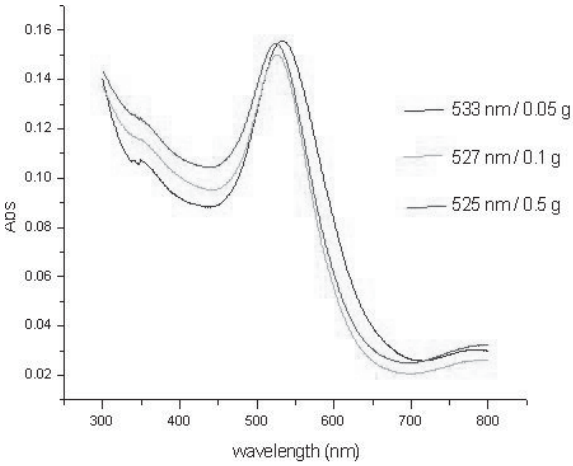

Fig. 2. UV/VIS spectra of various amounts of Au nanoparticles.

and thoroughly stirred. The mixing polyurethane resin was hardened with polyisocyanate, which consists of high reactive NCO groups. This group can react with the group of OH to form polymer compounds as the following chemical reaction.

$$R_1NCO + R_2OH \rightarrow R_1NHCO\,O\,R_2. \qquad (2)$$

The reaction can be rapidly hardened by curing and form the durable coating with high hardness. The ratios used for the composite were selected according to the low roughness of the paints.

Fig. 3 shows the dielectric permittivity with frequencies for the toluene with Au nanoparticles. Without the addition of Au nanoparticles, the pure resin is not responded to the electromagnetic frequency. On the other hand, the paints with the addition of Au nanoparticles have cut-off frequencies taking place at about $9.0 \cdot 10^8$ Hz. The permittivities of the paints with additions of Au nanoparticles oscillate and increase up to 83 F/m, especially for the addition of 6 ml. The results indicate that the addition of Au nanoparticles can alter the frequency property of the paints, and oscillate with the applied electromagnetic frequency. The oscillated response might be the interaction of the enhanced dipole field built up around metal nanoparticles with the electromagnetic field. Furthermore, the increase of the permitivities is not proportional to the amount of additions. This might imply that the coupling interference of the dipole field causes at high concentration of Au addition, and results in the shielding of polarized Au nanoparticles. With the proper addition of Au nanoparticles, the electromagnetic coupling between the particles can be optimized to increase the sensitivity to a weak change of the shallow dielectric environment [6]. Fig. 3b shows the imaginary parts of permittivities with frequencies for the paints with the Au nanoparticles. The response tendency is similar to that of the real parts. Nevertheless, the cut-off frequency responses delay to about $1.2 \cdot 10^9$ Hz. Again, the maximum imaginary permittivity of the paint is not proportional to the addition amount.

Fig. 4 shows the magnetic permeabilities with the frequency for the Au-imbedded paints. The magnetic responses show the same respond trend for the resins with and without Au nanoparticles. The cut-off frequencies take place at about $9.0 \cdot 10^8$ Hz. Nevertheless, the addition of Au nanoparticles in the polyurethane resin slightly increases the magnetic response. Fig. 4b shows the imaginary parts of magnetic permeabilities with frequencies. The magnetic responses show the same trend for the resins with and without Au nanoparticles. The cut-off frequencies also take place at about $9.0 \cdot 10^8$ Hz. There are no significant magnetic delays for those paints.

Fig. 5 shows the reflective losses calculated from the measured data shown in Figs. 3 and 4. The energy loss can be calculated according to the following equation [7].

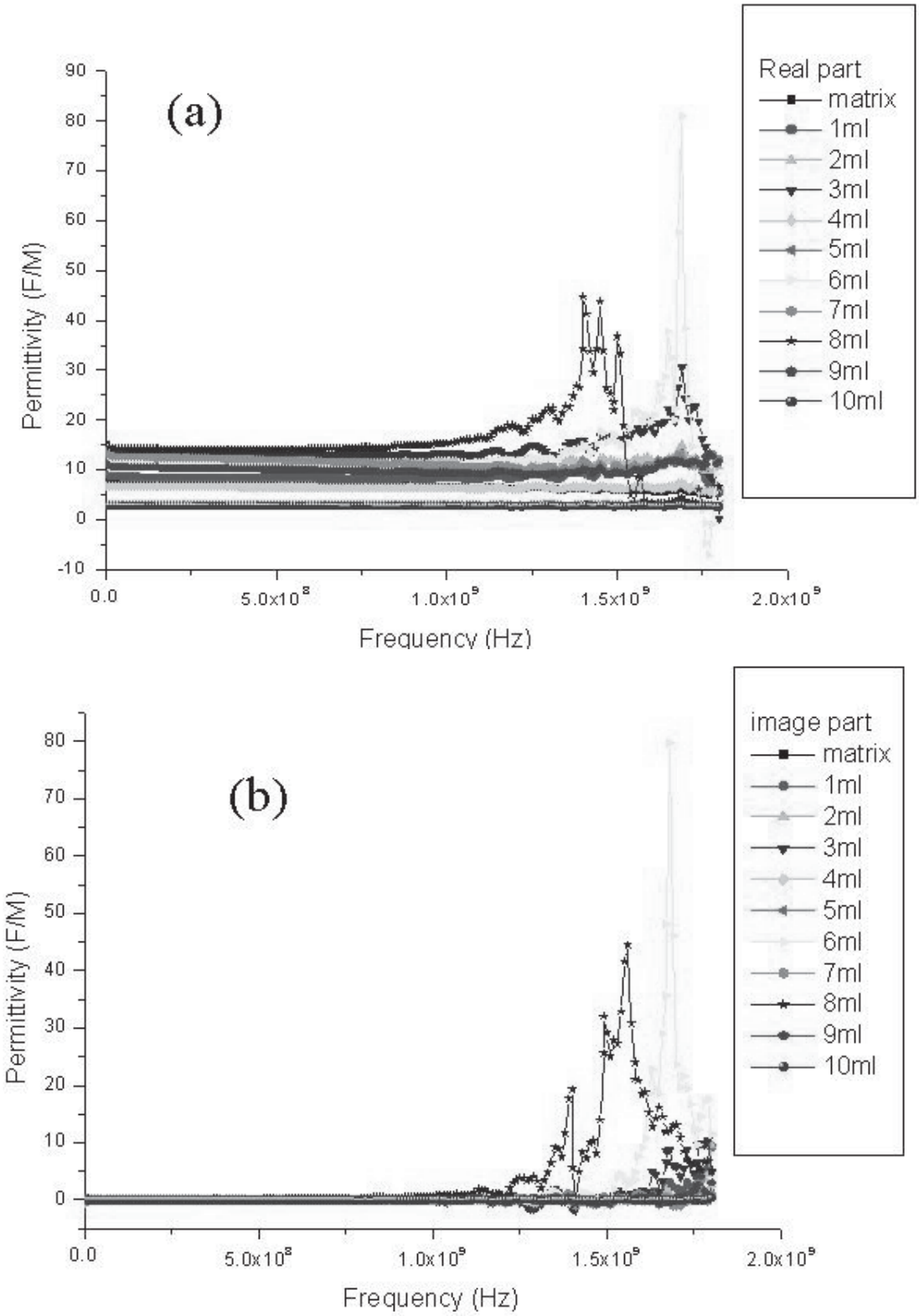

Fig. 3. The permittivities with frequencies for the Au nanoparticles imbedded in the resin. (a) real parts and (b) imaginary parts.

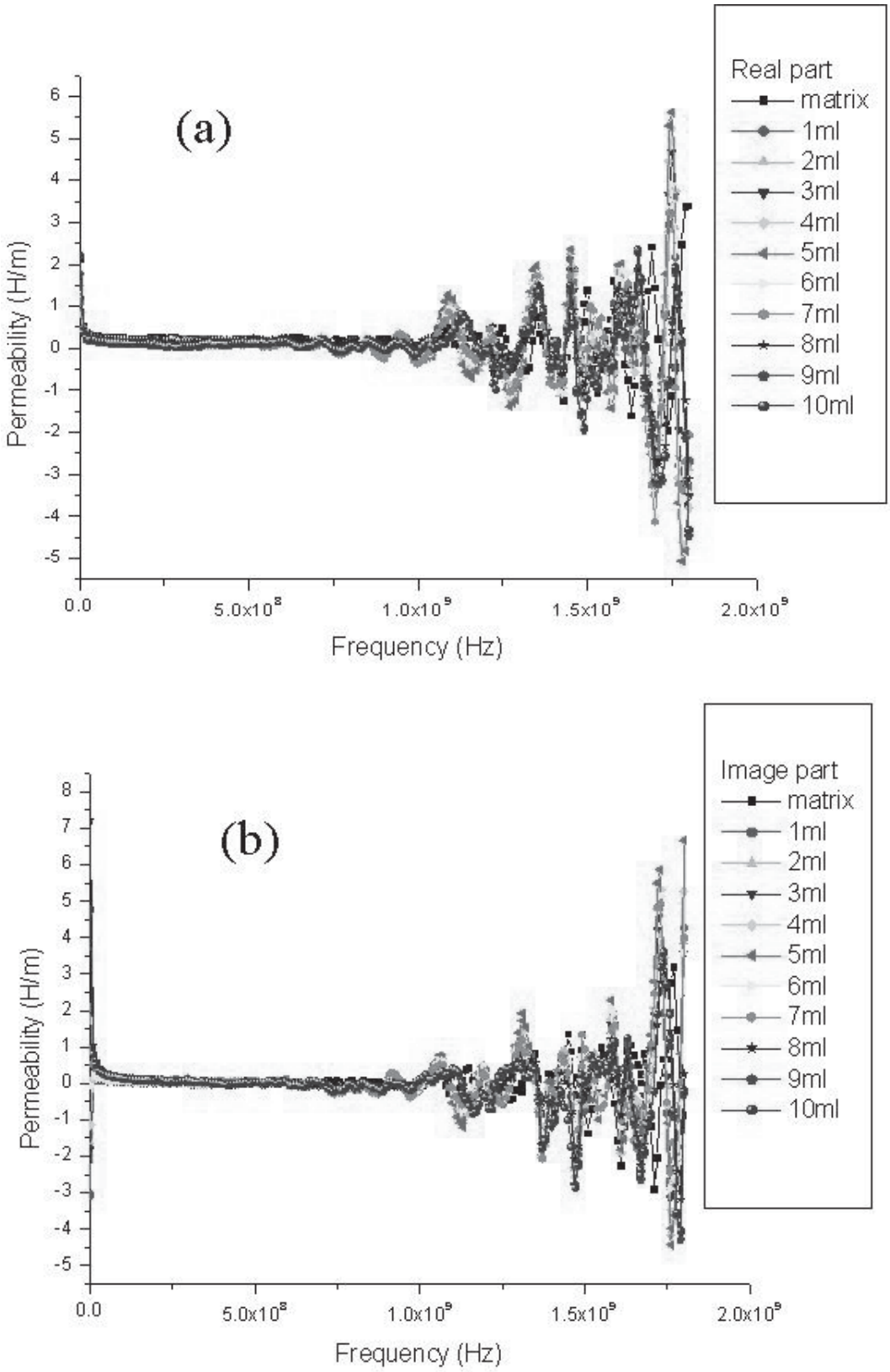

Fig. 4. The permeabilities with frequencies for the Au nanoparticles imbedded in the resin. (a) real parts and (b) imaginary parts.

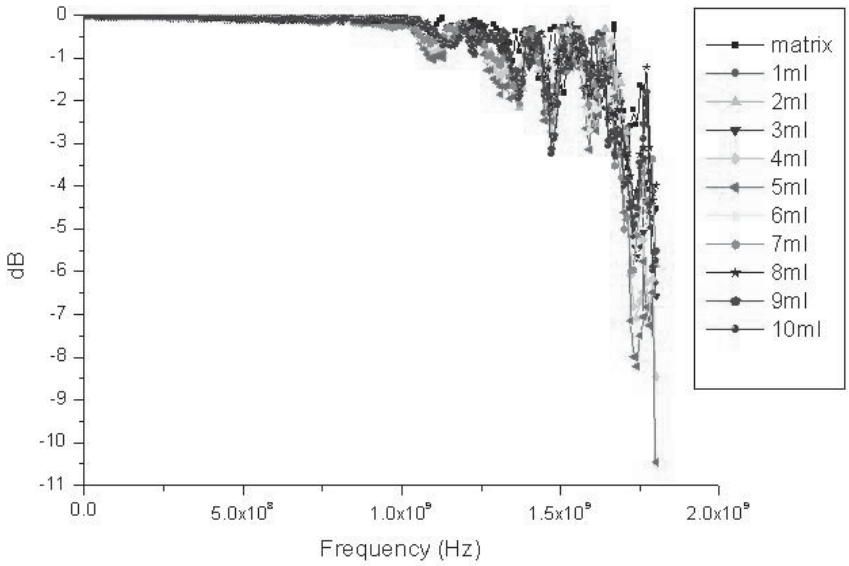

Fig. 5. Reflective losses for Au nanoparticles in polyurethane resin.

$$Z_{in} = \sqrt{\frac{\mu}{\varepsilon}} \tanh\left[\left(j\frac{2\pi}{C}\right)\sqrt{\mu\varepsilon}fd\right]. \quad (3)$$

Here, C is the light speed ($3 \cdot 10^8$ m/s), f is incidence frequency (1/s), d is the thickness of absorber. In this study, the paint thickness is about 1 mm. The real part of dielectric permittivity indicates the energy could be stored under external electrical field. The imaginary part is related to the loss of energy in the external electromagnetic field. The cut-off frequencies take place at about $9.0 \cdot 10^8$ Hz. The paint with the nanoparticle-imbedded solution of about 5 ml shows efficiently reflective loss at the frequencies of about $1.7 \cdot 10^9$ Hz within the measurable range. This implies that the fluctuation with frequency cause the energy exhausted by the various morphologies of the Au nanoparticles.

4. CONCLUSIONS

Au nanoparticles in polyurethane resin have shown the frequency responses. The permitivities and permeabilities of Au-imbedded resins fluctuate at the frequencies over about $9.0 \cdot 10^8$ Hz. The inherent response with the electromagnetic field causes the fluctuated relay especially at high concentration addition. The shielding from themselves on the high concentration of Au addition could retard the fluctuated response. The optimization between plasmon response and coupling effect causes high frequency response. As a result, the reflective losses take place at about $9.0 \cdot 10^8$ Hz for the paints and exhaust significantly at high frequency.

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