Optical behaviours of two dimensional Au nanoparticle arrays within porous anodic alumina

C Hsu and H H Liu

Department of Applied Chemistry & Materials Science, Chung Cheng Institute of Technology, National Defence University, Ta-Si, Taoyuan 335, Taiwan, R.O.C.

E-mail: hsen@ccit.edu.tw

Abstract. The optical responses of Au nanoparticle arrays dispersed within porous anodic alumina (PAA) have been investigated. The 2D Au/PAA structures were well preparing by immersing various pore sizes of PAAs into the mixing solution of HAuCl₄, cetyl-trimethyl ammonium bromide, and NaBH₄ under Au phase transfer processes. With the dispersion of Au nanoparticles in those nanopores in PAA, the intensity of photoluminescence light and cathodoluminescence light spectra largely decreases. The dissipated emission could be interpreted by the partly sealing of the light emission oxygen defect centers in PAA with the dispersion of Au nanoparticles. The major absorption comes from the interface plasmon resonance of Au nanoparticles surrounding with PAAs. The excited Au nanoparticles act as a Bragg grating for wave propagation scattering into the alumina matrix.

1. Introduction

Two-dimensional surface nanostructures have been demonstrated to play a role on the near-field optical properties [1-3]. The optical properties of two-dimensional metal nanoparticle arrays on various substrates not only arise from the excitation of a surface-plasmon resonance localized on individual metal nanoparticles but also from a propagating surface-plasmon wave from the interface of metal nanoparticles with the substrate. On the other hand, the spacing of metal nanoparticles can act as a grating coupler and therefore affects the resultant optical properties of two-dimensional arrays. It is therefore interesting to investigate the effect of surface nanostructures on the near-field optical spectroscopy. However, most of the works concern about oblate spherical Au nanoparticles deposited on various substrates. To the knowledge of the authors, the 2-D spherical Au nanoparticles imbedded in substrates are not mentioned in the literature. Because of this, in this study, the Au nanoparticles in-situ grown in porous anodic oxide alumina (PAA) and the resultant optical properties are revealed.

PAA provides two-dimensional nanoporous arrays, and been widely used as a template for fabricating various nanowires for the applications in semiconductor, optoelectronic, and magnetic [4-11]. The nanoporous structure of PAA formed by electrochemical anodic oxide in acid solution is regularly distributed and parallel with an average diameter range of 10 nm to 100 nm. The barrier layer is always formed on the bottom of the nanopores and the thickness is determined by anodic oxide voltage and time [12]. One of the characteristics of PAA is able to provide various light emissions. Blue light emission attributes to the singly ionized oxygen vacancies (F⁻ centers) at about...
413 nm [13,14], and oxygen vacancy F with two electrons (F centers) at about 430 nm. The PAA structure can be formed on the Si surface and be shown with extra light emission at 565 nm [15]. The light emission originates from optical transitions between the energy levels of F center with one positive charge. The Si-based PAA also showed ultraviolet and violet photoluminescence at 295 nm, 340 nm, and 395 nm [16]. In this study, the 2-D nanopores of pure PAA are imbedded with noble-metal Au nanoparticles which is in-situ grown by phase transfer method. The prepared nanostructure provides large proportion of Au surface area which is surrounded by alumina. In the surface mode region, the extinction peaks of Au particles take place near the Fröhlich frequency ($\lambda_f = 520$ nm) [17] in the nanoscale size. However, the surface plasmon wave of individual Au nanoparticles is not consistent with the light emitted from PAA. The interaction of the Au/PAA nanostructures with the excited emission from PAA is, therefore, proposed.

2. Experimental method

The PAA nanostructure was prepared by chemical anodic oxide method. The source material is aluminum foil with a purity of 99.9995 %. To release internal residual stress and initiate recrystallization, the samples were annealed at 400 °C for 1.5 hrs. The annealed samples were electropolished in the alcohol-perchloric acid with a mixing ratio of 5:1 at 10 °C under the anodic voltage of 17 V to remove the roughness of the annealed samples. The oxalic acid solution was used for the process of anodic oxide. The first anodic oxide was carried out at 7 °C under 50 V for 1 hours and cleaned with de-ion water. The first oxide was removed in the 6% H$_3$PO$_4$ solution mixed with 1.8% H$_2$CrO$_4$ at 60 °C for 10-15 mins. For the preparation of AAO, the second oxide was carried out at 7 °C for 1 hour and the other parameters were the same as the first step. The reaming process was carried out in phosphorous acid for 15 mins, 30 mins, and 45 mins at the potential voltage of 50 V. The various diameter and depth of nanopores were prepared by controlling pore-widening time. The samples were immersed in phosphorous acid mixed with chromium acid at the potential voltage of 50 V and kept at 7 °C. The prepared PAAs were immersed in the solutions for the nucleation and growth of Au nanoparticles which were prepared by phase transfer method [18]. 2 ml of 0.01 M 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. The 2-D Au/PAA surface nanostructures were observed in a scanning electron microscopy. The photoluminescence emission was measured by He-Cd laser with a wavelength of 325 nm as the excitation source. The CL emission was excited by electron beam with energy of 5 KV.

3. Results and discussion

Various pore sizes of PAA were manufactured for the subsequent nucleation and growth of Au nanoparticles. The pore sizes were controlled by the pore-widening time of 20 mins, 40 mins, and 60 mins respectively. The 2-D Au/PAA nanostructures were well prepared as shown in figure 1 showing a typical scanning electron microscopy image of Au nanoparticles within the PAA with the widening time of 20 mins. The Au nanoparticles are well nucleated and grown inside the nanopores of PAA. The pore size of PAA limits the nucleation and growth of Au nanoparticles in toluene solution. In this case, the average pore size of PAA is about 67 nm. The average size of Au nanoparticle is about 45 nm. The linear distance of pore neighbors is about 36-210 nm. In some nanopores, several Au nanoparticles formed in the same pores and contact with another. The shape of contact particles are deformed for the space confinement of nanopores during growth. From the point view of coupling, those particles in the same pores could increase the optical interaction of Au/PAA arrays. Figure 1(b) shows the cross section of Au/PAA structures. The Au nanoparticle is not sealed the whole nanopores. There are still have some internal surface presented.
Figure 1. Micrograph of Au nanoparticles dispersed in the porous anodic alumina with the widening time of 20 mins. (a) top view image; (b) cross section image.

The prepared 2D Au/PAA arrays were excited with different light sources as shown in figure 2. Figure 2(a) shows the PL optical spectra of pure PAA and 2-D Au/PAA arrays which were excited by a He-Cd laser with the wavelength of 325 nm. The PAA's with various pore sizes show the characteristics of light emission with a peak wavelength of 420 nm. These PL peaks of PAA's mainly arise from two kinds of oxygen vacancy centers, and the peaks are convoluted as a single peak. Those blue light emissions attributes to the singly ionized oxygen vacancies (F' centers) at about 413 nm, and the oxygen vacancy F with two electrons (F centers) at about 430 nm. The PL emissions of PAA's decrease with increasing the widening time. This could be explained by the decrease of the defect centers with increasing the widening time [14]. With the dispersion of Au in PAA, the PL spectra of the 2-D Au/PAA arrays dramatically decrease as shown in figure 2(a). The dissipated emission is different with the surface plasmon resonance peak in the Au nanoparticle solutions as our previous paper mentioned [19,20]. This implied that the extinction wavelength of 420 nm mainly attributes to the surface plasmon wavelength in the interface of Au metal nanoparticles with the PAA substrate.

The surface plasmon resonance occurs in the near-UV/visible region. The intensity is absorbed in proportion with increasing the pore size. The extinction could also come from the sealing of the pores with the dispersion of Au nanoparticles in PAA's. However, the nanopores are not fully sealed with Au nanoparticles. This implies that the main extinction mechanism mainly comes from the interface plasmon resonance. Figure 2(b) shows the CL spectra for PAA and 2D Au/PAA arrays. The acceleration voltage of the used electron beam for CL image is 5 kV. The excited wavelength of the PAA is close to the PL peak wavelength. With the dispersion of Au nanoparticles, the CL spectra of the 2-D Au/PAA arrays dramatically decrease as shown in figure 2(b). The extinction takes place at different excited source.

Figure 2. Optical spectra for 2D Au/PAA arrays. (a) PL spectra; (b) CL spectra.

Figure 3 shows the CL images of PAA and Au/PAA after pore-widening for 20 mins. Figure 3(a) show the uniformly sharp sub-micro bright light spots correspond to the excited centers from the PAA. With the dispersion of Au nanoparticles in 2D PAA array, the optical extinction of 2D Au causes no contrast of background. The CL image of the samples with the 2D Au arrays shows the black contrast. It demonstrates that the Au arrays extinct the light excited from the PPA. This implies that the bright wavelength of near 430 nm extinct to generate the surface plasmon resonance in the interface of Au nanoparticle with PPA.
The structure of 2-D Au/PAA arrays has large proportion of interface between Au nanoparticles and PAA. The interface facilitates the formation of the surface plasmon, and, as a result, causes the extinction of the emission of 420 nm from PAA. As a result, the surface plasmon is generated due to the excited emission from PAA. The surface plasmon generated from the interface can be estimated from a grating coupling mechanism. The surface plasmon propagating wavelength for a semi-infinite metal is given \[21\] by

\[
k_{sp} = \frac{\omega}{c} \left( \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2} \right)^{1/2} = \frac{\omega}{c} \sin \theta_i \pm mG
\]

In the equation, \(k_{sp}\) is the amplitude of the surface-plasmon wave vector, \(\omega\) the angular frequency of the incident light beam, \(c\) the speed of light in vacuo, \(\theta_i\) the incidence angle, \(m\) is an integer, \(G=2\pi/\Lambda\) the amplitude of the grating vector, \(\varepsilon_1\) and \(\varepsilon_2\) the dielectric functions of the metal and the surrounding medium, respectively. In this case of the spectra of gold particles in PAA, the calculations were performed using experimental gold dielectric function \[21\] and porous anodic alumina \[22,23\]. The predicted surface plasmon wavelength value of \(k_{sp}\) is about 278 nm. The grating length, \(\Lambda\), is about 278 nm for the zero incident angle. The optical properties of the 2-D Au/PAA arrays are schematically shown in Figure 4. The light emission from the PAA defect centers excites the surface plasmon of Au nanoparticle arrays. The generated surface plasmon can act as the new emission source in the wavelength form of ultraviolet light. From the point views of scattering, the Au nanoparticle arrays can be used as a new exciting source if underlying thin films can be excited \[2\]. In this study, the interface plasmon propagates into the PAA and the Aluminum substrate. The new generated wavelength of PAA from Au/PAA arrays could iteratively absorb from the 2-D Au/PAA nanostructures.

The electromagnetic coupling between the particles affects the optical property. The neighbor particle distance can be controlled by the pore-widening time. In general, the coupling decreases with increasing the distance. The distance can be controlled by the pore widening time. The coupling...
strength between particles depends on the propagation length, and decrease as \( \exp(-\alpha r)/r \), where \( \alpha \) describes the propagation length of the mode [2]. Some particles grow in the same nanopores, and form Au dimmers in PAA arrays. The near-field intensity show completely different field distributions compared to the case of a single particle array [3]. The dimmers-Au/PAA arrays could show different responses for larger nanopores with some Au dimmers.

4. Conclusions
The 2D-Au nanoparticle arrays in PAA were successfully prepared, and provided high ratio of interface surface area. The interface of Au nanoparticle within alumina dissipated the emission from PAA. The excited of 2D-Au nanoparticles acts as a Bragg grating for wave scattering propagation into the alumina matrix. The Au nanoparticle arrays can be used as a new exciting source if underlying thin films can be excited.

Acknowledgements
The authors would like to thank the financial project of from NSF of Taiwan under the project no of NSC94-2216-E-014-004 and 95-2914-I-014-001-A1. It also acknowledges the help of Prof. Kuei-Hsien Chen and Mr. Chih-Wei Hsu from the institute of atomic and molecular sciences on the work of the CL spectra and images. The helps on the PL works supported from Prof. J. L. Shen and Mr. K. W. Chen from Department of physics, Chung Yuan Christian University in Taiwan are also thankful.

References
[1] Palpant B, Prével B, Lermé J, Cottancin E, Pellarin M, Treilleux M, Perez A, Vialle J L and Broyer M 1998 Phys. Rev. B 57 3 1963
[2] Fé lidj N, Aubard J, Lé vi G J, Krenn R, Schider G, Leitner A and Ausseneegg F R 2002 Phys. Rev. B 66 245407
[3] Enoch S, Quindant R and Badenes C 2004 Opt. Exp. 12 15 3422
[4] Yang Y, Chen H, Mei Y, Chen J, Wu X and Bao X. 2002 Solid. State Comm. 123 279
[5] Wen W B, Zhu J J and Chen H Y 2003 J. Cryst. Growth 258 176
[6] Peng T, Yang H, Dai K, Pu X and Hirao K 2003 Chem. Phys. Lett. 379 432
[7] Jin C G, Liu W F, Xiang X Q and Cai W L 2003 J. Crys. Growth 258 337
[8] Kim L, Yoon S M, Kim J and Suh J S 2004 Syn. Met. 140 135
[9] Zhang H, Ma X, Xu J, Niu J, Sha J and Yang D 2002 J. Growth 246 108
[10] Xu D, Xu Y, Chen D, Guo G, Gui L and Tang Y 2000 Chem. Phys. Let. 325 340
[11] Shen C M, Zhang X G and Li H L 2001 Mat. Sci. Eng. 303 19
[12] Wang X and Han G R 2003 Microelect. Eng. 66 166
[13] Du Y, Cai W L, Mo C M, Chen J, Zhang L D and Zhu X G 1999 Appl. Phys. Lett. 74 20 2951
[14] Huang G S, Wu X L, Mei Y F, Shao X F and Siu G G 2003 J. Appl. Phys. 93 1582
[15] Huang G S, Wu X L, Xie Y, Shao X F and Wang S H 2003 J. Appl. Phys. 94 4 2407
[16] Wu J H, Wu X L, Tang N, Mei Y F and Bao X M 2001 Appl. Phys. A Mat. Sci. Proc. A72 735
[17] Bohren C F and Huffman D R 1983 Absorption and scattering of light by small particles (John Wiley & Sons, New York) p 370
[18] Brust M and Kiely C J 2002 Coll. Surf. 202 175
[19] Hsu C and Liou Y C 2005 Rev. Advan. Mat. Sci. 10 325
[20] Hsu C, He Y H and Chang C H 2006 Syn. React. Inorg. Metal-org. Nanomet. Chem. 36 281
[21] Raether H 1988 Surface plasmons on smooth and rough surfaces and on gratings (Springer, Berlin, Spring Tracts in Modern Physics vol 111) ed G Huhler
[22] Wäckelgärd E 1996 J. Phys. Cond. Matt. 8 4289
[23] Eriksson T S, Hjortsberg A, Niklasson G A and Granqvist C G 1981 Appl. Optics 20 15 2742