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T. Qiu, X. L. Wu, G. G. Siu, and Paul K. Chu

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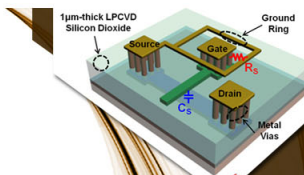
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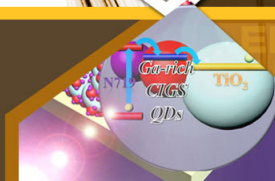
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# Self-assembled growth and green emission of gold nanowhiskers

T. Qiu<sup>a)</sup> and X. L. Wu<sup>b)</sup>

National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

G. G. Siu and Paul K. Chu<sup>b)</sup>

Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People's Republic of China

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Unique structured Au nanowhiskers were fabricated via electroless metal deposition on Si wafer in  $\text{KAuCl}_4\text{-HF}$  solution. A self-assembled localized microscopic electrochemical cell model and a diffusion-limited aggregation process are associated with the formation of Au nanowhiskers. A green photoluminescence (PL) band was recorded. Spectral analyses suggest the green PL arises from the radiative recombination of  $sp$ -band electrons with  $d$ -band holes in the Au nanowhiskers and its intensity enhancement is due to local electric field connected with the Au particle plasmons oscillation. A red PL band was also observed from long-time etched Si substrates and proposed to be related to Si nanocrystals in the surface layer of etched Si wafer. Its stability was considered to be owing to the formation of stable Si-Au bonds on the surfaces of Si nanocrystals. © 2005 American Institute of Physics. [DOI: 10.1063/1.2138360]

Recently, experiments have shown that there are surprisingly strong metal-metal interactions between gold atoms in molecular complexes,<sup>1</sup> and chemists have started to use them to design new structures with unusual physical properties.<sup>2</sup> The photoluminescence (PL) measurements of gold nanostructures are of importance in understanding electroluminescence device operating, where semitransparent gold electrodes are used.<sup>3</sup> Moreover, understanding optical processes in gold nanostructures may give important information regarding applications in surface-enhanced Raman scattering,<sup>4</sup> nonlinear optics,<sup>5</sup> and surface-enhanced fluorescence.<sup>6</sup> In this letter, we present a relatively rapid method of fabricating unique structured gold nanowhiskers via electroless metal deposition on Si wafer in  $\text{KAuCl}_4\text{-HF}$  solution. As compared with other strategies for gold nanostructural synthesis, mainly including photochemical synthesis,<sup>7</sup> template synthesis approach,<sup>8</sup> wet chemical synthesis,<sup>9</sup> electrochemical synthesis,<sup>10</sup> we believe that our methodology provides a simple and convenient route to a variety of building blocks for assembling noble metals with novel structure and function in nanotechnology.<sup>11</sup> A green PL band has been recorded and considered to be due to the radiative recombination of  $sp$ -band electrons with  $d$ -band holes in the Au nanowhiskers.

The sample fabrication method is described as follows: A  $p$ -type, B-doped silicon (100) ( $1\text{--}5\ \Omega\ \text{cm}$ ) wafer was first cleaned by acetone to degrease the Si surface, followed by etching in diluted aqueous HF solution for 10 min. Then the cleaned silicon wafer was cut into four pieces. They were etched in a 5.0 mol/L HF solution containing 0.02 mol/L  $\text{KAuCl}_4$  at 50 °C for 30, 10, 1 min, and 5 s, respectively. The container is a conventional Teflon-lined stainless steel vessel. After the etching process, the four silicon wafers were rinsed with de-ionized water and blown dry in air. The morphology and chemical composition of the

samples were examined with a FEG JSM 6335 field emission scanning electron microscope (SEM) and a PHI 5600 x-ray photoelectron spectrometer (XPS) with monochromatic Al  $K\alpha$  source at 14 kV and 350 W. The photoelectron take-off angle was 45°. Powder x-ray diffraction (XRD) spectrometer was used to characterize the gold nanostructures. Data were collected on a Japan Rigaku D/Max-RA x-ray diffractometer with Cu  $K\alpha$  radiation ( $\lambda=0.1542\ \text{nm}$ ). The PL measurement was performed on a T64000 triple Raman system (Jobin-Yvon Company) using the 488 and 514 nm lines as excitation sources. All the measurements were performed at room temperature.

The morphologies of the gold nanostructures are etching-time dependent, as shown in Fig. 1. At the initial

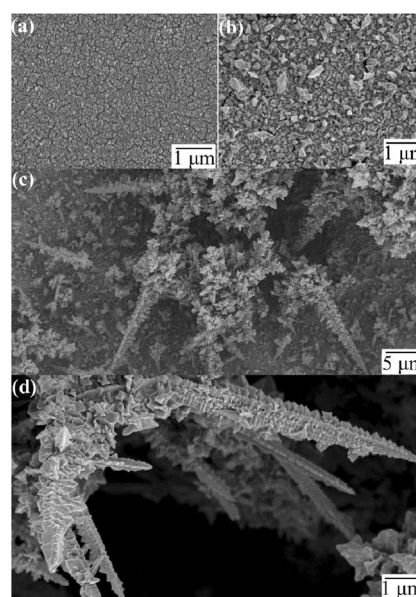


FIG. 1. SEM images of the gold nanostructures grown on silicon wafers via electroless metal deposition in a 5.0 mol/L HF solution containing 0.02 mol/L  $\text{KAuCl}_4$  at 50 °C. The etching time is (a) 5 s, (b) 1, (c) 10, and (d) 30 min.

<sup>a)</sup> Also at: Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, People's Republic of China.

<sup>b)</sup> Authors to whom correspondence should be addressed; electronic mail: hxxlwu@nju.edu.cn, paul.chu@cityu.edu.hk

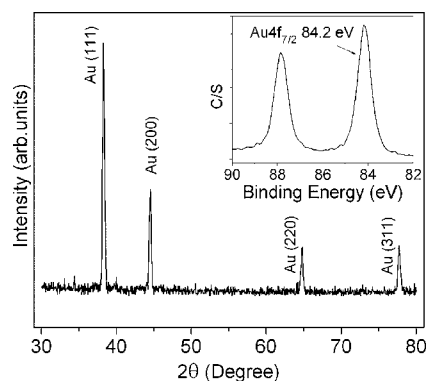


FIG. 2. XRD pattern of the as-prepared gold nanowhiskers shown in Fig. 1(d). The inset shows the binding energy position of Au  $4f_{7/2}$  at 84.2 eV.

stage, the deposited gold atoms first form nuclei and then form nanoclusters which distribute on the surface of the silicon wafer to form a continuous film [Figs. 1(a) and 1(b)]. After etching for 10 min, change has obviously taken place on the surface of the silicon wafer [Fig. 1(c)]. Many gold nanoclusters diffuse and stick together to form whisker-like nanostructures. This can be more clearly seen in the 30 min etched Si wafer [Fig. 1(d)]. The diameters of the nanowhiskers are nonuniform and in the range of 0.1–1  $\mu\text{m}$ . Their maximal lengths can reach about 10  $\mu\text{m}$ . Typical powder XRD patterns of the nanowhiskers are shown in Fig. 2. The four diffraction peaks can respectively be indexed to the (111), (200), (220), and (311) planes of fcc gold (JCPDS 04-0784). The corresponding XPS spectrum of the gold nanowhiskers with Au  $4f_{7/2}$  signal at 84.2 eV, shown in the inset of Fig. 2, displays additional proof.<sup>12</sup>

The formation of the gold nanowhiskers can be understood on the basis of self-assembled localized microscopic electrochemical cell model and diffusion-limited aggregation process (DLA).<sup>13,14</sup> At the beginning, the silicon etching and gold deposition occur simultaneously at the silicon surface. The deposited gold atoms first form nuclei and then form nanoclusters which uniformly distribute on the surface of the silicon wafer [Fig. 1(a)]. These gold nanoclusters and the Si areas surrounding these gold nuclei could, respectively, act as local cathodes and anodes in the electrochemical redox reaction process.<sup>15</sup> We believe that the electrochemical cell model is similar to that of forming Si nanowire arrays in the case of Ag deposition.<sup>15,16</sup> That is to say, many small flat honeycombs form around one tiny deposited gold nanocluster. Numerous nanosized honeycomb-like anodes and one gold nanocluster acting as local cathode form an electrochemical cell.<sup>16</sup> These cells could be self-assembled on the surface of the silicon wafer. To prove this process and give direct evidence of the cell model, the etched Si wafers were treated in an ultrasound water bath to remove the deposited gold nanostructures and only leave the residual Si substrates, as shown in Fig. 3. It can be seen that the honeycombs become larger and deeper with increasing the etching time. Further etching of intermediate honeycombs will lead to the formation of special shaped Si nanowires.<sup>16</sup>

The synchronous growth of gold nanowhiskers should be considered within the framework of a DLA model, which involves in cluster formation by the adhesion of a particle with random path to a selected seed on contact and allows the particle to diffuse and stick to the growing structure.<sup>14</sup> *In situ* prepared honeycombs around the gold nanoclusters

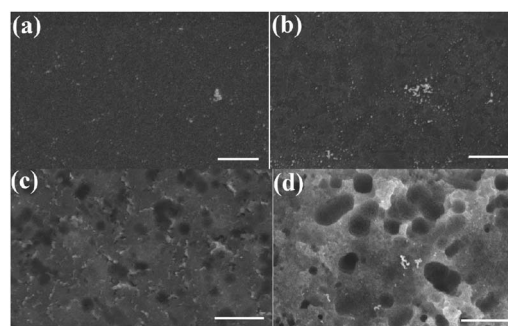


FIG. 3. SEM images (scale bar: 1  $\mu\text{m}$ ) of residual silicon substrates etched in HF-KAuCl<sub>4</sub> solution with different times: (a) 5 s, (b) 1, (c) 10, and (d) 30 min.

could be regarded as the template that is something like Xiao's work about ultrasonically assisted template synthesis of palladium and silver dendritic nanostructures.<sup>17</sup> During the initial stage, high concentration of the gold salt and reduction agent lead to reduction-nucleation growth of gold nanoclusters at a lot of positions to form chainlike network. With prolonging reaction duration, the concentration of gold salt and reduction agent greatly decrease, the growth is mainly driven by decreasing surface energy and thus the whisker-like gold nanostructures are formed.

The PL spectra of the gold nanostructures, taken under excitation with the 488 nm line of an Ar<sup>+</sup> laser, are presented in Fig. 4(a). The emission peaks at  $\sim 550$  nm are centered near the interband absorption edge of bulk gold.<sup>18</sup> Optically excited metal surfaces show no or very little luminescence.

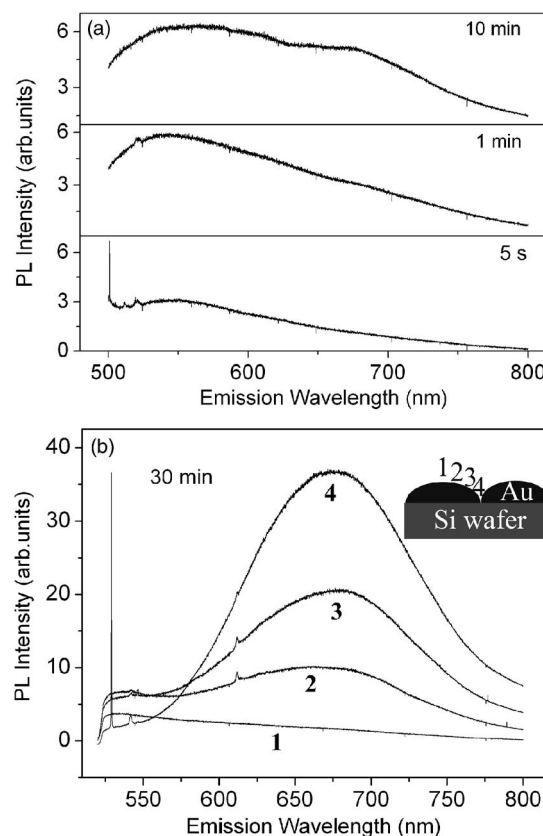


FIG. 4. PL spectra of the gold nanostructured films on silicon wafers etched in HF-KAuCl<sub>4</sub> solution with different times ( $\lambda_{\text{ex}}=488$  nm) and (b) different illumination positions of laser beam ( $\lambda_{\text{ex}}=514$  nm). The inset shows a schematic diagram of the illumination points.



For instance, smooth gold films show a PL with very low efficiencies of  $\sim 10^{-10}$  following excitation of electron transitions from the  $5d$  to the  $6sp$  bands.<sup>18</sup> In other words, only one photon is emitted under excitation of per  $10^{10}$  electron-hole pairs. One likely reason for this low PL efficiency is that nonradiative energy relaxation processes of photoexcited carriers in metals, such as Coulomb carrier-carrier scattering, are much faster than radiative electron-hole recombination, thus quenching the PL.<sup>19</sup> A unique exception from the rule of low PL yields in metals is noble-metal nanoparticles. For example, PL efficiencies on the order of  $10^{-4}$  have recently been observed in gold nanorods.<sup>20</sup> The origin of this effect is being argued.<sup>19–22</sup> Conceivably, the enhancement is caused by an acceleration of the radiative process in the nanoparticles as compared to the bulk, due to size-dependent screening effects which accelerate electron-electron scattering<sup>23</sup> and lead to emission by hot carriers of particle plasmons, i.e., collective oscillations of the conduction electrons.<sup>24,25</sup> In our experiments, intensity of the green PL is enhanced in rougher gold nanostructured films. Thus, we suggest that the intensity enhancement of the green emission from the radiative recombination of  $sp$ -band electrons with  $d$ -band holes is due to local electric field associated with the gold particle plasmons oscillation.

Here, it should be mentioned that the PL from long-time etched Si substrates themselves cannot be ignored. A broad emission band centered at  $\sim 680$  nm can clearly be seen in the sample etched for 10 min, as shown in Fig. 4(a). Chen *et al.*<sup>26</sup> have reported that the PL intensity from Au-passivated porous Si nanocrystals can be enhanced due to the formation of stable Au–Si bonds at the surface of Si nanocrystals. Our PL spectrum is similar to that in the literature. Therefore, we believe that the red PL band arises from Si nanocrystals with surface Si–Au bonds. To identify the PL mechanism, we made the following experiments: Fine adjust the position of the sample using microscopic monitor and let laser beam illuminate a gold particle ( $\sim 50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ ) from center to edge found on the surface of 30 min etched Si wafer, as schematically shown in the inset of Fig. 4(b) by points 1–4, and then collect the PL signal. Figure 4(b) shows the corresponding PL spectra, taken under excitation with the 514.5 nm line of Ar<sup>+</sup> laser. It can be seen that the intensity of the 680 nm emission is position dependent. The PL from point 4 is the strongest and the PL from point 1 has vanished. If we consider the limited penetration depth of laser beam, the red PL can be understood to be from Si nanocrystals and its intensity increase from points 1 to 4 is due to the increased density of luminescent Si nanocrystal. Meantime, the existence of stable Si–Au bonds also leads to stability of the Si nanocrystal surface.<sup>26</sup> As a result, the red PL peak position remains unchanged with the sample storage history in air.

In summary, a rapid, inexpensive method of fabricating gold nanowhiskers has been described on the basis of electroless metal deposition technique. The formation of the gold nanowhiskers can be interpreted on the basis of self-assembled localized microscopic electrochemical cell model and DLA process. A green PL band is observed at 550 nm.

PL spectral analyses suggest that the green emission arises from the radiative recombination of  $sp$ -band electrons with  $d$ -band holes and its intensity enhancement is due to local electric field associated with the gold particle plasmons oscillation. A red PL band was also observed from long-time etched Si substrates and proposed to be related to Si nanocrystals in the surface layer of Si wafer. Its stability was considered to be owing to the formation of stable Si–Au bonds on the surfaces of Si nanocrystals.

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