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Full Length Article

Conductive scanning probe microscopy of the semicontinuous gold film and its SERS enhancement toward two-step photo-induced charge transfer and effect of the supportive layer

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ABSTRACT

The semicontinuous gold film, enabling various electronic applications including development of surface-enhanced Raman scattering (SERS) substrate, is investigated using conductive atomic force microscopy (CAFM) and Kelvin probe force microscopy (KPFM) to reveal and investigate local electronic characteristics potentially associated with SERS generation of the film material. Although the gold film fully covers the underlying silicon surface, CAFM results reveal that local conductivity of the film is not continuous with insulating nanoislands appearing throughout the surface due to incomplete film percolation. Our analysis also suggests the two-step photo-induced charge transfer (CT) play the dominant role in the enhancement of SERS intensity with strong contribution from free electrons of the silicon support. Silicon-to-gold charge transport is illustrated by KPFM results showing that Fermi level of the gold film is slightly inhomogeneous and far below the silicon conduction band. We propose that inhomogeneity of the film workfunction affecting chemical charge transfer between gold and Raman probe molecule is associated with the SERS intensity varying across the surface. These findings provide deeper understanding of charge transfer mechanism for SERS which can help in design and development of the semicontinuous gold film-based SERS substrate and other electronic applications.

1. Introduction

Surface-enhanced Raman scattering (SERS), amplifying the weak Raman signal by taking advantages of interactions between the incident light and roughened metal surfaces, has opened up various fields of application development such as biomedical diagnostic [1,2], forensic identification [3,4], catalysis process [5,6], and solar cells [7,8]. Electromagnetic mechanism (EM) and chemical mechanism (CM) are the two processes for signal enhancement of SERS. In electromagnetic mechanism (EM), long-range effect, plasmonic oscillation resonance of conducting electrons in roughened surface amplifies the incident light wave and consequently increases Raman scattering intensity of the analyst molecule. Factors affecting the enhancement include surface morphology (e.g. surface roughness [9,10], size of rough features [10–12], and nanostructured patterns [13–16]) and plasmonic absorption of substrate and probe molecule [11,12,17]. On the contrary, chemical mechanism (CM) is short-range effect with the enhancement generated by transfer of conducting electrons between SERS substrate and Raman analyst. Configuration of molecule on substrate [18], their electronic structure [19], and substrate-molecule distance [20] affect the charge transfer activity. The estimated EM enhancements in the range of 10^4–10^8 have been reported while less contribution in the range of 10^0–10^3 is commonly noted for CM. It is however an ongoing debate for fundamental understanding of each mechanism and its contribution magnitude; especially for the ultrathin film, as well as the 2D material, possessing flat and smooth surfaces [17,19,21].

Since both EM and CM involve surface topography, optical characteristic, and charge distribution of the metallic thin film, obtaining these data is compulsory for understanding of SERS. Scanning electron microscopy and atomic force microscopy are the gold

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standards to characterize surface morphology with nanoscale resolution [9,11,12,22]. Meanwhile, information on electronic structure and plasmonic absorption can be respectively obtained using ultraviolet photoelectron spectroscopy and UV–Visible spectroscopy [12,17,23], in which data is collected from a spot size in range of a few hundred nanometers. Since the traditional techniques have not enabled to acquire these characteristic data simultaneously, the topographical information can only be indirectly correlated to the electronic and optical information at the same spatial location. This methodology complicates interpretation of data toward the underlying mechanisms of SERS.

Considering that both SERS mechanisms rely on surface conducting electrons and the enhancement activity is a pure localized effect, together with the attempts to build relations between optical characteristic and electronic property of materials [24,25], direct observation of nanoscale electronic properties of SERS surface would shed more light onto both enhancement mechanisms and relevant characteristics of SERS substrate. Conductive atomic force microscopy (CAFM) and Kelvin probe force microscopy (KPFM), which can provide simultaneous mapping of local topography and conductivity of material surface with nanoscale spatial resolution and consequently give insights toward application of the material [26–33], would be suitable tools for such the local electronic characterization.

Here, we propose to use the scanning probe microscopy (SPM) techniques to simultaneously obtain surface topography and the corresponding electronic distribution on SERS substrate surface. The semicontinuous gold film-based SERS substrate is chosen as the primary target for this combined CAFM and KPFM analysis because: the gold film is one of the materials of choice in SERS development considering its simple fabrication method while producing large SERS active area, the gold is highly stable and has biocompatible potential, its relatively flat surface will enable accurate SPM imaging and allow elucidation of EM and CM separately, and moreover the film does not only find application in SERS but it is also applicable in other fields of electronic development [34–38]. Nevertheless, in thin film-based SERS development, since film thickness has been considered an important SERS-affecting factor which can also influence surface morphology and even plasmonic absorption [23,39–41], the semicontinuous film (specifically ~10 nm thick) is comparatively investigated with other ultrathin gold films of different thickness so that its enabling size-dependent characteristic can be realized.

2. Experimental methods

2.1. Sputtering fabrication

N-type silicon (Semiconductor Wafer, As-doped, resistivity 0.001–0.005 Ω·cm, orientation ⟨0 0 1⟩) was cleaned by sonicating for 10 min in each of the following solvents; acetone, de-ionized water, isopropanol, and ethanol, respectively. Gold films having thickness of 50 nm, 30 nm, 10 nm, 5 nm, and 1 nm were then deposited on the silicon substrates covered by native SiO_2 using DC sputtering under high-vacuum (Leica, Mikrosysteme GmbH) at a deposition rate of 0.05 nm/s.

2.2. SPM characterization

SPM (Hitachi Hi-Tech, SPA400 and JPK, NanoScience) was used to characterize morphology and electronic properties of the gold films under ambient conditions. Gold-coated silicon tips (TipsNano, CSG01/Au) were used in conductive-AFM mode for which bias is applied to the sample. A platinum-coated tip (Bruker, OSCM-PT-R3, k = 2 N/m) was used for Kelvin probe force microscopy mode in which the sample is grounded while the nullifying bias is applied to the tip. Before KPFM measurement, work function of the Pt-coated tip was found to be 6.6 eV based on the contact potential difference between the tip and freshly cleaved highly ordered pyrolytic graphite (HOPG) (NT-MDT, work function 4.6 eV).

2.3. SERS measurement

Methylene blue of 10^{-4} mol/L (Sigma–Aldrich, Fluka 66,720) and aqueous reduced graphene oxide of 0.5 mg/mL (Graphenea) were used as Raman analyst molecules. A 3 μL was dropped on each gold surface and dried overnight under ambient condition. Raman spectra of the probe molecules collected from random locations on the surface were obtained using Raman Spectrometer (NT-MDT, NTEGRA Spectra) with a green laser of 532-nm wavelength. Mapping Raman spectroscopy (Renishaw, inVia) was also performed in which we utilized the same acquisition condition for each mapping pixel as used in the point Raman spectroscopy.

3. Results and discussion

3.1. CAFM characterization

Fig. 1(a)–(e) shows morphology and the corresponding electrical signal taken from the 50-nm, 30-nm, 10-nm, 5-nm, and 1-nm gold films using CAFM. Considering topography images, although each film fully passivates the silicon surface with roughness of only ~1.5 nm (also see Fig. S1), their surface grains are different in shape and size such that the films can be divided into three groups and film growth can be described based on the Volmer-Weber growth literature [42] as follows. Group I comprises 1-nm and 5-nm films, Group II is 10-nm film, and Group III consists of 30-nm and 50-nm films. For the 1-nm and 5-nm gold films, the growth follows the Volmer-Weber mode in which a small amount of deposited metal atoms on the native SiO_2 layer forms isolated clusters with increasing tensile stress of the film. As the film deposition proceeds, the isolated clusters coalescence to form larger clusters and eventually irregularly-shaped islands of arbitrary sizes as observed in the 10-nm gold film, which is in good agreement with prior reports on surface morphology of the semicontinuous gold film [12,17,35,43,44]. For the 30-nm and 50-nm film growth, adatom diffusion on the basal layer of deposited metal prevails instead of the cluster coalescence with film compressive stress built up. The random islands completely transform to circular-shaped and uniform-sized smaller grains.

Regarding the current images, insulating voids (less than tip dimension of ~35 nm in curvature radius) appearing towards dark color in the positive-bias images and towards white color in the negative-bias images are observed throughout surface of the 50-nm, 30-nm, and 10-nm films. They can be attributed to the loose electrical tip-sample contact corresponding to small vertex and steep contour of the surface. However, this is not the case for the larger insulating islands which are distributed throughout the 10-nm gold film and appear at the same locations even when the surface is re-scanned at different sample biases as shown in Fig. 1(c). (See Fig. S3 for different areas of the 10-nm film surface revealing the island-like insulator.)

Based on the CAFM images and the measurement configuration, it reveals that although the 10-nm gold film consisting of surface grains of random shape and size fully passivates the silicon semiconductor, this morphologically-random film is electrically semicontinuous. The gold film is composed of a large and continuous conductive region – the bright area in the positive-bias image or the dark area in the negative-bias image – decorated with the