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SERS-active Ag/Au bimetallic nanoalloys on Si/SiO_x

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ABSTRACT

Nanoalloys are clusters formed of two or more metallic elements and are of interest for applications in catalysis, spectroscopy, photonics, electronics, and magnetism. The hybridization of the individual plasmonic absorptions of different alloyed metals allows for plasmon tunability and a better coupling of plasmon-excitation line, giving rise to significant increases in the enhancement factor for surface-enhanced Raman scattering (SERS) spectroscopy. Here we report simple fabrication procedures for the preparation of Ag/Au nanoalloys on Si/SiO_x substrates, with tunable plasmon resonances. The mechanism and kinetic of the nanoalloy formation and its optical properties were studied by SEM, XPS, SPR, and SERS.

1. Introduction

Surface enhanced Raman scattering (SERS) has been receiving a great deal of attention as a powerful analytical technique because of its potential use in a wide range of applications, including biomolecular recognition [1], macromolecular characterization [2], and ultra-sensitive detection [3]. Although originally reported in electrodes in electrochemical cells, the SERS effect has been studied in two types of nanostructured systems, namely colloidal dispersions of metal particles and nanostructured metal films [4]. The nanostructured films approach provides SERS substrates with some advantages relative to the colloidal systems, such as portability, tunability, and compatibility with a wider range of substrates. The functional property of the substrate itself, for example when it is used as an optical waveguide, can be advantageously used to expand the fields of use and increase the detection limits of this powerful analytical tool.

Since the realization that physical properties of metallic nanoparticles (MNP) and their nanoscale dimensions are connected through quantum confinement effects, there has been great interest in using them as building blocks for the fabrication of new materials with enhanced optical properties. Two general approaches emerged over the past few years to combine metals on the nanoscale. The first consists in generating ordered arrays of MNP via self-assembly [5], and the other consists in fabricating nanoalloys. In the latter case, laser-assisted synthesis of Au–Ag alloy nanoparticles in solution [6], galvanic substitution of a vacuum evaporated Ag island film with Au on Nafion [7], fungi-mediated Au/Ag nanoalloys [8], core-shell Ag/Au alloys using galvanic substitution in solution [9], and other wet-chemical methods were reported [10]. Alloy nanoparticles exhibit unique and often enhanced electronic, optical [7,11], and catalytic [12] properties relative to the corresponding individual MNPs [13].

Most of the solution-phase experiments in SERS are performed using either Ag or Au nanoparticles. Ag nanostructures can provide large enhancement in Raman intensities, but they are unstable under physiological conditions. In contrast, Au nanostructures are stable in biological systems, but they provide moderate enhancement in SERS experiments [14]. Thus, Ag/Au bimetallic nanoalloys are interesting target materials since they can combine the benefits of the surface properties of Au with the optical enhancing properties of Ag. In addition, the development of alloy nanostructures is attractive because they allow for the formation of effective hot-spots, and because of their composition-dependant optical properties originating from the hybridization of the plasmonic absorptions of the different materials involved [9].

Here we report simple procedures for fabricating Ag/Au alloy films on Si/SiO_x substrates, which are very effective for SERS analysis. Film growth was monitored by field emission scanning electron microscopy (FESEM), X-ray photoelectron spectroscopy (XPS) and surface plasmon resonance (SPR). The SERS properties of the films were characterized using 2-naphthalenethiol (NAT) as an analyte. We have chosen Silicon because it is an excellent material for con-

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fining and manipulating light at the sub-micrometer scale. Silicon photonics has been the subject of intense research activity in both industry and academia [15]. In intrinsic single crystal bulk Silicon, light with wavelength longer than the Si bandgap wavelength ($\lambda_g = 1.107$ μm) can propagates with a low loss. Particularly attractive is the high refractive index contrast (HIC) of Si waveguides. In such HIC waveguides, light is highly confined in the core which can have cross-sections as small as ~250 nm and bending radii can be reduced to a few micrometers. Ultra-compact planar waveguide devices can hence be made in Si. Recently, Si waveguide photonic devices for spectroscopy [16] and sensing [17] have been reported with potential applications in SERS. It is thus of considerable interest to extend the plasmon resonances of SERS substrates into the transparency range of Si.

2. Materials and methods

All chemicals and solvent were obtained from Aldrich and used as received. Sacrificial Ag films of 9, 15 and 21 nm mass thickness on commercial electronic grade Si/SiO_x wafers were prepared in a Kurt J. Lesker 4-pocket electron beam evaporation unit. During the film deposition the background pressure was 10^{-6} Torr, and the deposition rate (0.5 Å s^{-1}) was monitored using an XTC Inficon quartz crystal oscillator. Ag/Au bimetallic films were prepared by immersing the Ag island films into a solution of $KAuCl_4$ (50 mL, 10^{-3} M) over different time periods. After the galvanic reaction the samples were thoroughly rinsed with deionized water then dried under a stream of N_2 in a desiccator. Formation of the nanoalloys was monitored by surface plasmon resonance spectroscopy (Perkin–Elmer Lambda 35 equipped with a diffuse reflectance accessory at a 45° angle), field emission scanning electron microscopy (Hitachi S4800), and X-ray photoelectron spectroscopy (Axis 165 XPS, Kratos Analytical). The SPR spectra were monitored over 168 h and no significant changes were noted over this time period. Silver oxide may have formed during this process, but XPS data suggests that it is minimal.

Samples for SERS analysis were prepared by casting 10 μL of a 10^{-4} M solution of 2-naphthalenethiol (NAT) on the fabricated films. The inelastically scattered radiation was collected on a Nicolet Almega system equipped with a CCD detector, an optical microscope, and a 780 nm laser line. All measurements were made in backscattering geometry, using a 50× microscope objective, providing scattering areas of 1 μm^2. Spectra were collected in high-resolution mode with accumulation times of 2 s. Ten different points were probed for each surface. SERS mapping of the edges of the Si/SiO_x wafers was obtained under similar conditions, but using a single grating, an accumulation time of 1 s and step size of 0.5 μm^2.

3. Results and discussion

Sacrificial Ag films present different topographies as a function of their initial mass thickness (Fig. 1). The 9 nm Ag film presents typical ellipsoidal MNPs with size varying between 40 to 70 nm [18]. As the film grows in mass thickness, the MNPs coalesced into a discontinuous film. Notably, both the 15 and 21 nm Ag films are characterized by small Ag protuberances between 10 to 50 nm. After immersion in the Au(III) solution, all three films show an agglomeration into larger nanostructures ranging in size from 50 to 500 nm. Formation of bimetallic nanoalloys by galvanic substitution has previously been described in colloidal suspensions by Xia and co-workers [19]. In this case, the same galvanic replacement process takes place on the Si/SiO_x surface. Au(III) oxidizes Ag as it is retained on the surface according to this reaction:

$$3Ag(0) + [KAu(III)Cl_4] \rightarrow 3Ag(I) + Au(0) + 4Cl^- + K^-.$$

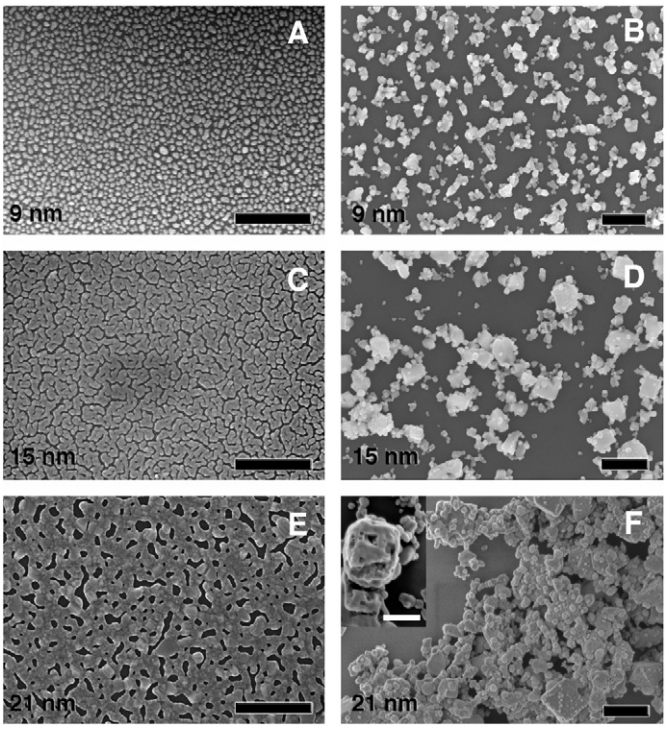

Fig. 1. SEM micrographs of the Ag sacrificial films (A, C, E) and their Ag/Au nanoalloys (B, D, F). The inset in (F) shows the pinholes in the Ag/Au alloys. The heights of 9, 15 and 21 nm in (A), (C), and (E) refer to the mass thickness of an equivalent smooth film as measured with the quartz crystal oscillator. Black scale bars = 500 nm, white scale bar = 200 nm.

During this oxidation process, the more electropositive metal (i.e. Ag(I) ions) solubilizes while new Au(III) atoms are reduced (Au(0)) and diffuse into the metallic structure to form the alloy. Because three Ag atoms are required for each Au atom, the oxidation of surface Ag in the clusters by the Au(III) solution would require Ag migration to the surface generating pinholes, which are clearly observed in Fig. 1F (inset). These observations are in agreement with recent insights into the dealloying theory by Erlebacher and co-workers [20] and Dixon et al. [21].

Remarkably, Ag, Au and all Ag/Au bulk alloys exhibit a fcc packing [22] arrangement with similar atomic sizes (1.45 and 1.44 Å, respectively) and lattice constants (0.409 nm and 0.408 nm, respectively) suggesting the formation of a homogeneous solid for virtually any alloy compositions [23]. Moreover, Ag has a lower surface energy (78 meV $Å^{-2}$) than Au (95 meV $Å^{-2}$), which facilitates the diffusion of Ag atoms to the surface of the alloy [24]. This favors a continuous replacement of the material yielding a homogeneous alloyed solid rather than a segregated bimetallic material.

The bimetallic nature of the nanoalloys was established by XPS (Fig. 2). Sacrificial Ag films show fundamental bands at 368.2 eV ($3d_{5/2}$) and 374.2 eV ($3d_{3/2}$), with no evidence of the presence of Au. After immersion, Ag 3d bands decreased in intensity while metallic Au 4f bands at 84.4 eV ($4f_{7/2}$) and 88.1 eV ($4f_{5/2}$) increased. A shift to lower binding energies was also observed in both Ag 3d and Au 4f fundamental bands as the Au concentration increased in the nanoalloy. This phenomenon has previously been reported by Rao et al. and is consistent with the generation of a bimetallic nanoalloy in the film [25].

Surface atomic composition was determined by XPS measurements. Fig. 3 shows Au molar fraction as a function of the immersion time of the film into the Au(III) solution. Notably, the adsorption of Au onto the Ag films shows a hyperbolic trend with the adsorption rate decreasing with time, yielding adsorption maxima with atomic percentages of retained Au of 10.7, 13.5 and 17.6%