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Surface-enhanced infrared absorption studies of copper nanostructures formed by oblique-angle deposition

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ABSTRACT

It is demonstrated that Cu nanostructures fashioned by oblique angle deposition (OAD) of gaseous Cu atoms onto CaF_2 substrates have SEIRA enhancement factors that are close to par with Ag or Au nanostructures formed using vapor deposition at a normal deposition angle. Cu nanostructures grown at normal angle show about 5× in SEIRA enhancement of a *p*-nitrobenzoic acid (PNBA) monolayer and have a range of over 100 nm in particle size. Conversely, Cu nanostructures deposited by OAD show SEIRA enhancement of approximately 40× and are more uniform with approximate circular shapes averaging 25 nm and spacing less than 10 nm.

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1. Introduction

The coinage metals are the most popular substrates for surface-enhanced Raman spectroscopy (SERS) and surface-enhanced infrared absorption (SEIRA) including Ag, Cu, and Au [1–3]. These metals have the potential for plasmonic activity over a broad range of the electromagnetic spectrum [1–3]. In SEIRA experiments, it is thought that Cu is inferior to Ag and Au in terms of relative enhancement factors, possibly due to rapid Cu oxidation [4]. As such, SEIRA manuscripts involving Cu are limited in comparison to the volume of publications concerning Ag and Au [4–18]. The best SEIRA enhancement factors reported to date on Cu nanostructures (CuNSs) are 12–25× in an electrochemical environment to control potential Cu oxidation [4]. It is now common the use SERS and SEIRA together to study layer by layer growth of thin films adsorbed in proximity to metal nanostructures [19–31]. Such a long-range effect in SEIRA experiments brings into question the role of Cu oxidation in suppressing SEIRA in adsorbed organic or biological layers on CuNSs. Recently, it has been show that well organized, gold nanoshell aggregates have led to SEIRA enhancement factors of up to 4000× induce by surface plasmons from dipolar resonances [32]. Other metamaterials have been shown to have discrete plasmon activity in narrow windows in the mid-infrared region [33].

Here we will show that CuNSs grown in vacuum at an oblique deposition angle with respect to the metal source are superior to conventional CuNSs formed at a normal deposition angle (no substrate tilt with respect to the metal source). Application of oblique-angle deposition (OAD) has led to improved SEIRA substrates for Ag and Ni nanostructures [19,25,34]. SEIRA active Ag and Ni nanostructures formed by OAD have a more uniform distribution than Ag and Ni nanostructures fashioned at a normal deposition angle [25,32]. Recently, it was also established that CaF_2 and BaF_2 are more effective base substrates for the formation of SEIRA active metal nanostructures versus other conventional infrared transparent materials such as Ge, KRS-5, ZnSe, and AMTIR [20].

2. Methods

PNBA (98% pure) was purchased from Aldrich. Solvents used in solution preparation were HPLC or Optima grade (Thermo Fisher or Aldrich). The 25 × 4 mm polished CaF_2 windows were purchased from International Crystal Laboratories. The 99.9% pure Cu powder was purchased from Johnson Matthey Electronics. SEIRA and attenuated total reflectance Fourier transform infrared spectroscopy spectra were obtained on a Thermo-Nicolet IR100 FTIR spectrometer. All infrared spectra were conducted in transmission mode (2–

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4 cm^{-1} resolution; 16 scans were averaged). CuNSs were grown on CaF_2 by thermal evaporation of Cu as measured with an Infinicon quartz crystal microbalance in a home-built vacuum chamber with a base pressure less than 1×10^{-6} Torr. CaF_2 crystals were polished with a silica suspension, rinsed and sonicated in methanol, and dried in air. An approximate monolayer exposure of PNBA was prepared for SEIRA and SERS studies by pipetting 25 µL of a 50 ppm PNBA/acetone solution onto a Cu film and allowing the solvent to evaporate. This is approximately a monolayer assuming an experimentally determined average spot size of 4 cm^2 for all solvents, resulting in a reasonably uniform layer of about 250 ng/cm^2 with SEIRA enhancement factors that decrease by less than 2× toward the edges of the PNBA film. The monolayer here accounts for the number of PNBA molecules in a given area on a flat surface and does not consider surface roughness.

3. Results

Fig. 1A is an atomic force microscopy (AFM) image of 4 nm of Cu evaporated onto a CaF_2 window at a normal deposition angle. It is important to understand that 4 nm is not the Cu film thickness but rather the mass of deposited Cu as measured by a quartz crystal microbalance (QCM) in a geometrically equivalent position to the base CaF_2 substrate. Notice that the CuNSs in Fig. 1A has a large polydispersity with a particle size distribution greater than 100 nm. Fig. 1B is an AFM image of 50 nm of Cu deposited onto CaF_2 at an oblique-deposition angle of 75°. The 50 nm of Cu represents a mass of Cu measured on a QCM at 0° (no tilt) with respect to the metal deposition source. Compared to the CuNSs in Fig. 1A, the CuNSs in Fig. 1B are more evenly distributed in terms of size, shape, and spacing. Many of the CuNSs in Fig. 1B are semicircular with an average diameter of 25 nm and spacing of approximately 10 nm range. Fig. 1A has a root mean square (RMS) surface roughness of 3.071 nm and Fig. 1B has an RMS surface roughness of 0.936 nm. These characteristics have been shown to be important in obtaining the best SERS and SEIRA enhancement factors [35].

Fig. 2 is a representation of the formation of CuNSs from the evaporation of Cu at an angle normal to the base CaF_2 substrate and at a grazing angle (OAD). CuNSs formed at a grazing angle are more uniform in size and spacing because of the "shadowing effect" resulting from OAD [19,25,32]. As a secondary effect, the lower Cu exposure to the CaF_2 during OAD might also allow more time for the CuNSs to form and account for more Cu being evaporated using OAD to obtain CuNSs.

Fig. 3 is an infrared spectrum obtained in transmission mode of the CuNSs formed from the evaporation of 50 nm of Cu at 75° OAD (see AFM in Fig. 1B). A clean CaF_2 substrate was used for the background. Note the broad absorbance from 1200 to 4000 cm^{-1} including more pronounced bands in the 1200–1600 cm^{-1} range. Sharp bands in the range 2300–2400 cm^{-1} are from background CO_2 and were impossible to subtract out from the spectrum experimentally while simultaneously flooding the chamber with nitrogen to eliminate atmospheric water contributions. In the early days of SEIRA, it was assumed that the enhancement effect was due to tailing of the surface plasmon resonance from the visible into the infrared region [3–8]. More recent theories suggest that the SEIRA effect might be caused by the dielectric constant and optical extinction coefficient of the film [36,37]. As such, in Fig. 3 absorption from the CuNSs, and corresponding SEIRA enhancement discussed in Figs. 4 and 5, are likely due to a combination of these effects.

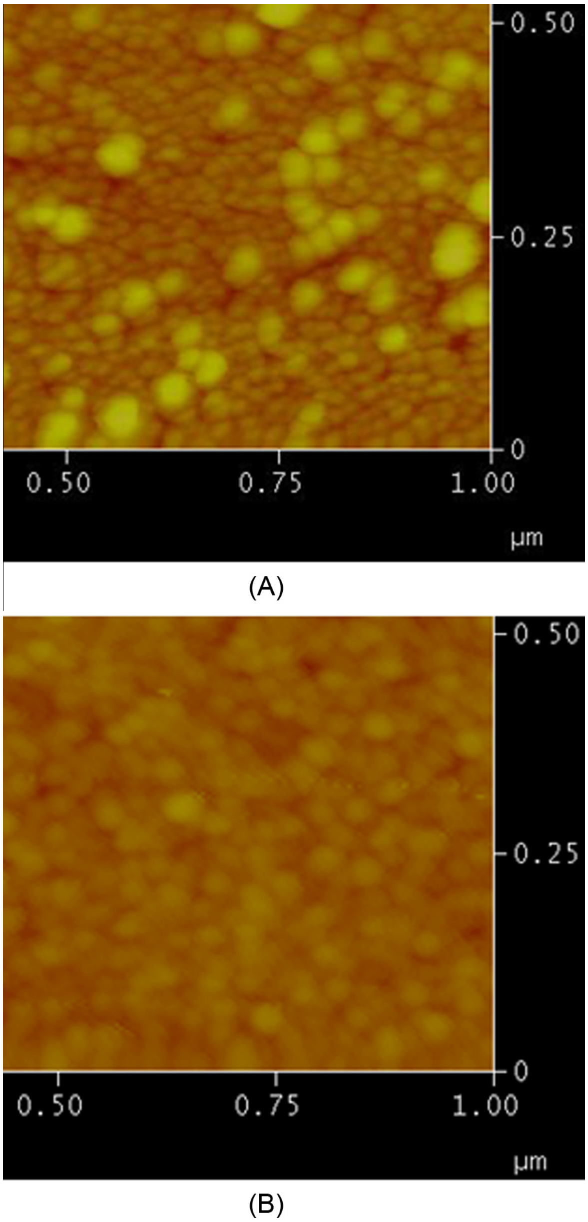

Fig. 1. A. AFM image of 4 nm of Cu evaporated on a CaF_2 substrate at a normal angle. B. AFM image of 50 nm of Cu evaporated onto a CaF_2 substrate at a 75° grazing angle.

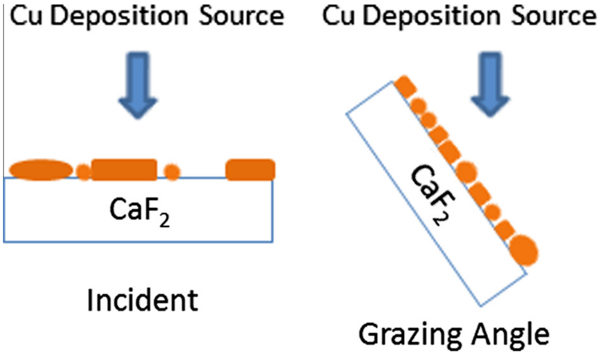

Fig. 2. Pictorial description of metal evaporation processes.

Fig. 4 displays typical infrared spectra obtained in transmission mode of approximately one monolayer (250 ng/cm^2) of *p*-nitrobenzoic acid (PNBA) deposited onto various substrates. Since Hartsein's original SEIRA experiments, PNBA has become an unofficial standard by which SEIRA enhancement factors are compared [19–21]. It is well known that PNBA adsorbs onto coinage metal substrates as a *p*-nitrobenzoate ion (PNBI) with the carboxylate

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