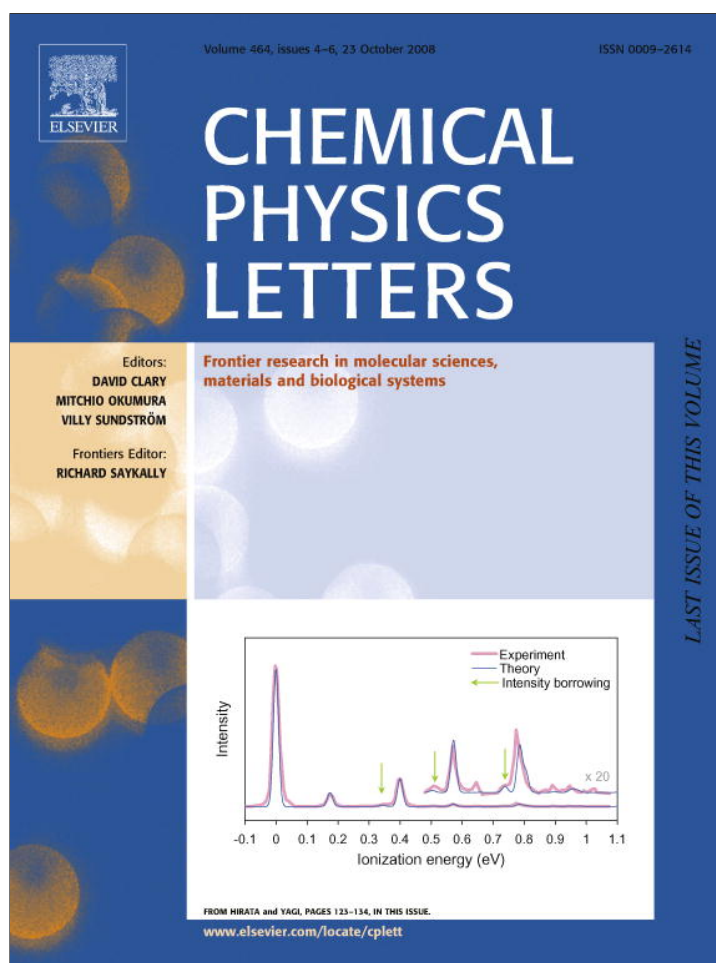


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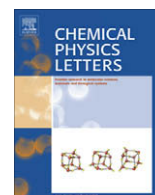
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Silver island nanodeposits to enhance surface plasmon coupled fluorescence from copper thin films

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ABSTRACT

A method to enhance surface plasmon coupled fluorescence (SPCF) from thin copper films using silver islands as an overlayer is presented. Silver islands were deposited onto copper thin films using a wet chemical technique for up to 60 s, which resulted in surface features ranging from randomly sized silver nanoparticles to a silver thin film. Theoretical Fresnel calculations predict the coupling of light to copper thin films with a silver overlayer. SPCF and the free-space emission intensities from Rhodamine B spin-coated onto silvered copper were found to be significantly larger than measured from the copper thin films alone.

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1. Introduction

Surface plasmon coupled fluorescence (SPCF) is a powerful technique that offers highly directional and polarized luminescence measurements to be performed from thin metal films [1,2]. The SPCF technique has found use in many luminescence-based bioassays to date [2–5]. Although SPCF was initially demonstrated with gold thin films [2] several other metals such as silver, aluminum [6], copper [7] and zinc thin films [8] have been employed each with their unique optical properties.

SPCF is related to the widely known surface plasmon resonance (SPR) phenomenon and thus affords for the utilization of the available SPR tools, such as the prediction of surface plasmon-light interactions for SPCF [9]. The reader is referred to the original paper by Knoll and Liebermann [1] for detailed information about the phenomenon. In SPR, the interaction of light with thin metal films can be precisely predicted using Fresnel calculations, which accounts for both the absorption and the transmission of light by the surface plasmon supporting metal thin films. Since only p-polarized light induces the surface plasmons on the thin films (when passed through a prism, Kretschmann configuration), one can combine the luminescence and the SPR technique by employing luminescent species as the near-field light source that interacts/induces the surface plasmon polaritons (PSP) in a non-radiative fashion, which is the crux of the SPCF technique [1,2]. Furthermore, the excitation of the luminescent species can also be achieved either directly from the air side (reverse Kretschmann

configuration). Both configurations described above can be employed in analytical sensing applications [4,5]. It is important to note that SPCF technique is different than another commonly used technique called localized surface plasmon resonance spectroscopy (LSPR) [10]. In SPCF, while PSP are induced on a thin metal film by light or fluorescence emission and coupled emission is emitted at a narrow angle from the back of the films, LSPR is responsible for electromagnetic field enhancements near metallic nanoparticles that lead to enhanced Raman scattering and enhanced resonances.

One can find several reports in the literature on the use of metal nanoparticles in combination with metal thin films to increase fluorescence [11], phosphorescence [12] and Raman signatures [13,14]. These reports are based on the use of the same metal combination (silver-on-silver or gold-on-gold, etc). In all of these reports, the increased signatures were thought to be due the plasmon coupling between the metal nanoparticles themselves as well as the plasmon coupling between the nanoparticles and the underlying metal thin film [12,13]. The use of metal nanoparticles along with the same underlying metal thin films can introduce several benefits to SPCF, such as increased fluorophore/luminophore photostability, increased SPCF as well as the free-space emission. On the other hand, one can find only a single report on the combined use of silver and gold *bimetallic continuous thin films* to increase evanescent fields for SPR-based biosensing applications by Ong et al. [15]. However, no reports on the use of different metal nanoparticle-thin films in combination with fluorophores for SPCF have been reported to date.

In this study, the use of silver islands to enhance the SPCF from copper thin films is reported. Silver island nanodeposits were deposited on 40 nm copper thin films using a wet chemical technique. This simple procedure yielded a silver overlayer with features ranging from random silver nanoparticles to silver thin

Abbreviations: MEF, metal-enhanced fluorescence.; SIFs, silver island films; SPCF, surface plasmon coupled fluorescence.

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films on top of the copper thin films. Scanning electron microscopy was employed to characterize these silvered copper thin films. Theoretical Fresnel calculations were also employed to predict the angle and the extent of coupling of light (at the same wavelength of Rhodamine B emission), which was subsequently confirmed with experimental data. In this regard, Rhodamine B was spin-coated from a polymer solution onto the silvered copper thin films and the SPCF and free-space emission was measured using an experimental rotational stage built in-house. It was shown that silver islands that were deposited for 50 s onto copper thin films yielded the largest increases in SPCF as well as the free-space emission. The angle of SPCF emission was also found to be shifted to smaller angles as predicted by the Fresnel calculations. Since silver is known to efficiently couple to light in the visible spectral region, the use of silver islands is also expected to broaden the wavelength of light or luminescence emission more towards visible wavelengths than can couple to copper thin films alone. The *silver-copper bimetallic combination* has enormous implications for SPCF-based bioassays than can be carried out using fluorophores emitting over a broad range of wavelengths on a single assay platform.

2. Materials and methods

Forty nanometer thick copper thin films were deposited onto Silane-prep glass microscope slides (Sigma–Aldrich) by AccuCoat, Inc (Rochester, NY). Silver island films (SIFs) were deposited onto copper substrates using a modified version of the previously published preparation procedure [16]. In short, silver nitrate is reduced by sodium citrate and ammonium hydroxide as previously described [16]. In the last step of the procedure, the copper substrates were inserted and kept in the reaction vessel for 20, 30, 50 and 60 s, respectively. The presence of silver islands deposited onto copper substrates was verified by scanning electron microscopy (SEM).

An aqueous solution of Rhodamine B (1 mM) was mixed with an aqueous solution of 10% PVA (w/v) to prepare a fluorophore/polymer mixture used to spin coat copper substrates. PVA films are used to homogeneously distribute fluorophores on copper substrates as a thin polymer film to study SPCF from such fluorophore/polymer/metal architecture. The final concentration of Rhodamine B was 0.01 mM in 1% PVA. Forty microliters of fluorophore/polymer solutions were subsequently spin-coated onto copper substrates (2.5 cm × 2.5 cm) using a Chemat Technology Spin Coater (Model KW-4A) with the following speeds: setting 1:8 s, setting 2:20 s. Since the thickness of the polymer film spin-coated onto metal films is dependent on the size of the support, and the

type and the settings of the spin coater itself, similar solution preparation conditions and settings were used to reproduce the results presented in this study. Under similar conditions, the thickness of a PVA film spin-coated onto silver surfaces from a 1% PVA solution was determined to be ≈ 37 nm [17].

Samples were excited using a reverse Kretschmann configuration that has been previously described [18]. All SPCF measurements were made with an Ocean Optics HD2000 Spectrofluorometer and a 600 μ m fiber that was mounted on a rotation stage that could be rotated 360° around the sample. Fresnel calculations were performed using a macro procedure written for Igor Pro software.

3. Results and discussion

Fig. 1 shows the SEM images for copper thin films coated with SIFs deposited for 20 and 60 s. Fig. 1 – insets depict the layering of the metals with respect to each other. In both SEM images copper and silver appear as dark gray and gray, respectively. For a 20 s deposition time, the SIFs appear as randomly deposited structures, similar to those observed on glass substrates reported earlier [19], on the copper thin films as shown in Fig. 1A. As the copper thin films are incubated in the silver island forming mixture, for up to 60 s, more silver islands are deposited onto the copper thin films forming a thin silver overlayer, cf. Fig. 1B.

Surface plasmon coupled fluorescence was previously shown for 40 nm copper thin films [7]. In addition, the preferential coupling of p-polarized light (over s-polarized light) in the red spectral region to copper thin films was also shown [7]. Building on these previous results, in this study, Fresnel calculations were carried out to predict the effect of silver and polymer (PVA, used to spin-coat the fluorophores) overlayers on the reflectivity of light from copper surfaces, and are shown in Fig. 2. To correlate the theoretical calculations later with the experimental results for Rhodamine B that has a fluorescence emission at 590 nm, the Fresnel calculations were subsequently carried out for light also incident at 590 nm. Fig. 2A shows that the minimum reflectivity for p-polarized light from 40 nm copper thin films with a 40 nm PVA overlayer occurring at $\approx 60^\circ$. The addition of a silver overlayer (and a subsequent PVA overlayer) on the copper thin films results in the shifting of the angle of minimum reflectivity to smaller angles, and more importantly, resulting in the narrowing of the reflectivity curve implying that coupled light will be detected from copper substrates at narrower angles. This prediction is not surprising considering the fact that the reflectivity curve for silver is sharper as compared to copper substrates [17]. In addition, the angle of

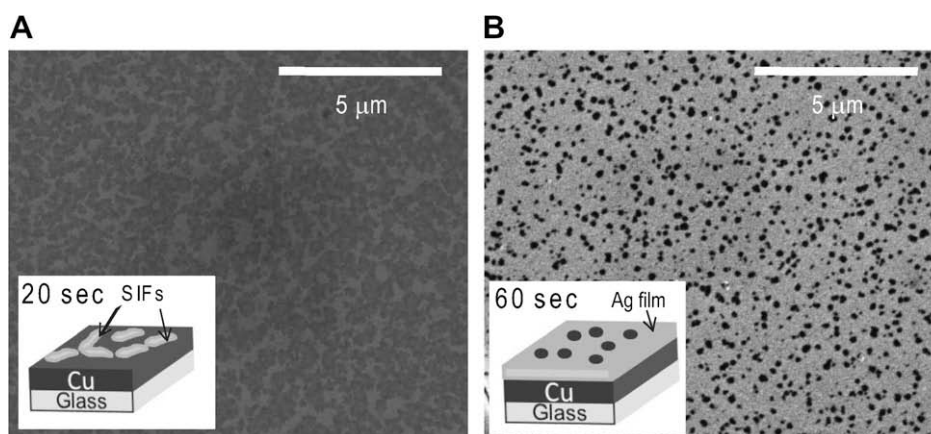


Fig. 1. Scanning electron micrograph (SEM) images for 40 nm thick copper thin films coated with silver island films (SIFs) deposited for (A) 20 s, (B) 60 s. Inset in (A) depicts the position of SIFs (gray, on top) and the copper thin film (dark gray, bottom) with respect to each other.

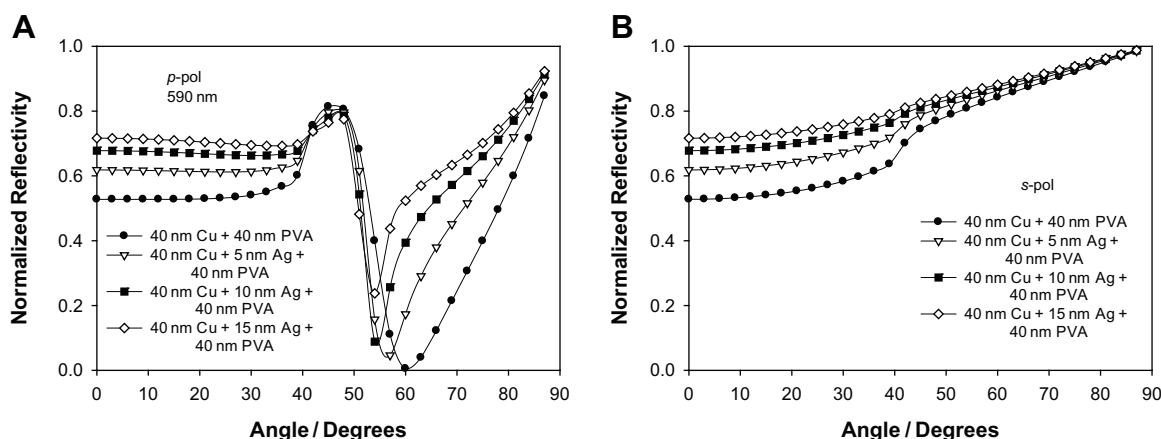


Fig. 2. Fresnel reflectance curves of (A) p-polarized and (B) s-polarized 590 nm light for both copper thin films and copper thin films coated with different thicknesses of SIFs, as well as 40 nm PVC film.

reflectivity minimum for silver occurs at around an angle of $\approx 50^\circ$ [17]. Fig. 2B predicts the reduction in the extent of s-polarized light as more silver is deposited onto copper substrates, which significantly increases the ratio of p- to s-polarized light, thus, potentially increasing the sensitivity of any fluorescence-based bioassays constructed on these bimetallic thin films, i.e., highly polarized directional emission.

Next the correlation of these theoretical predictions with the experimental evidence that SPCF can be further enhanced with silver overlayer was undertaken. Fig. 3 shows the angular distribution of the SPCF intensity (p-polarized) of Rhodamine B measured at 590 nm from copper thin films alone (a control sample) and copper substrates with various silver overlayers. The maximum SPCF intensity (50 arbitrary units) from copper thin films occurs at $\approx 62^\circ$ as predicted by the Fresnel calculations. The angle of the maximum SPCF intensity shifts to 57° , 56° , 53° and 52° , for copper thin films with silver islands deposited for 20, 30, 50 and 60 s, respectively. In addition, the SPCF intensity was 6-fold larger for copper thin films with silver islands deposited for 50 s (Cu + Ag - 50 s, in the graph) and the SPCF intensity from other silvered samples were comparable to the SPCF intensity from copper thin films alone. It is interesting to note that the SPCF intensity from copper thin films with silver islands deposited for 60 s is measured at a broad range of angles ($45\text{--}70^\circ$). This is thought to be due to the increased thickness of the silver overlayer that appears as a continuous thin film on the copper metal (Fig. 1B) with nanoscale

holes. This bimetallic nature of silver/copper substrates results in the transmission of coupled light (or fluorescence) at broader angles. Since the reflectivity minimum angle for silver and copper thin films is around 50° and 60° , respectively, the observation of SPCF intensity at a broader range of angles is not unexpected.

It is important to comment on the possible mechanism for the above observations, which can be explained in terms of the plasmon coupling between the silver nanoparticles and the copper thin films. The irradiation of the silver nanoparticles in close proximity with light induces surface plasmons in the silver nanoparticles, which in turn induce and couple to surface plasmons in the copper thin films. The coupling of surface plasmons results in new plasmon modes, which is effected by the plasmon wavelength of the silver nanoparticles. Since the surface plasmon wavelength of silver nanoparticles is blue-shifted with respect to copper surface plasmons, the new coupled plasmon modes include the plasmon modes from both the silver and the copper films. Depending on the size or the thickness of the silver nanoparticles/thin films, the angle of minimum reflectivity shifts towards smaller angles due to the interaction of incident light with silver metal. In addition, the electric fields above the copper thin films are significantly increased due the presence of silver nanoparticles/thin films, which results in increased coupling of light/emission to the copper films and thus, the SPCF intensity is further increased.

One important advantage of SPCF over the free-space fluorescence measurements is the detection of p-polarized light from

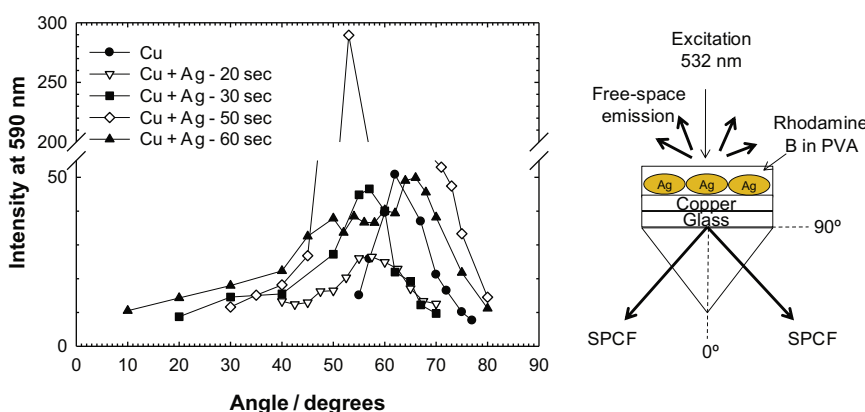


Fig. 3. SPCF intensity (measured at 590 nm) versus detection angle plots of 10 mM Rhodamine B in 1% PVC on copper thin films 40 nm thick with SIFs of variable surface coverage. The times in the legend refer to the time that the copper thin films were kept in the silver island forming solution (Tollen's silver mirror reagent). Note: the intensity axis is broken due to the intense signal observed for the 50 s sample and the need to see the intensity vs angle data for the other samples. The experimental setup is depicted on the right.

the back of the metal thin films, which arises from the preferential coupling of p- over s-polarized light to the surface plasmons [1]. In addition, the presence of plasmonic nanoparticles on the surfaces of the metal thin films was shown to further increase the fluorescence [11], phosphorescence [12] and Raman signatures [13]. In this regard, the effects of the presence of silver islands near copper thin films on the ratio of p- over s-polarized light (p/s) and the free-space emission is investigated and these results are summarized in Figs. 4 and 5. The results from the copper thin films with silver islands (Cu + Ag) were compared to those obtained from copper thin films without the silver overlayer (Cu, a control sample). Fig. 4 shows an increase in the p/s ratio for most of the Cu + Ag substrates, where the largest increase was observed for 50 s of silver island deposition (Cu + Ag – 50 s). It is interesting to note that for the samples with silver islands deposited for 20 s, the p/s ratio is decreased and the free-space emission is increased (Fig. 5). Since the silver islands formed on copper thin films for 20 s are similar to those which form on glass substrates where metal-enhanced fluorescence (MEF) is typically observed, the increase in the free-space emission for these samples is thought to be due to the MEF phenomenon [19,20], described extensively by our research group. In addition, since the copper thin films act a mirror, most of the otherwise transmitted emission is reflected from the copper thin films into the free-space. On the other hand, as more silver is deposited onto the copper thin films (silver becomes a thin film),

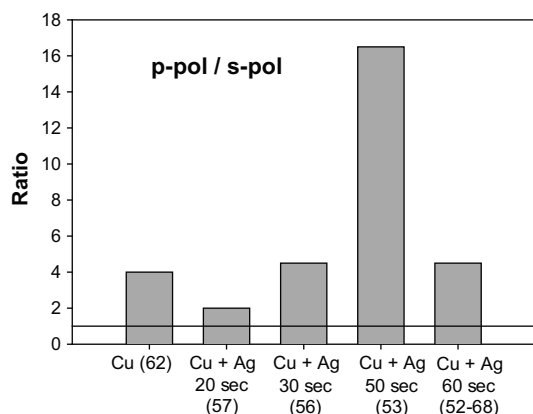


Fig. 4. Maximum p/s ratio of 10 mM Rhodamine B in 1% PVC deposited on copper thin films 40 nm thick with SIFs of variable surface coverage. Detection angle is noted in parentheses.

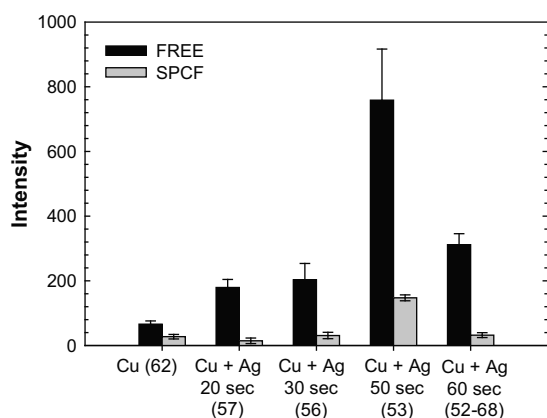


Fig. 5. Maximum SPCF and free-space emission intensity of 10 mM Rhodamine B in 1% PVA on copper films 40 nm thick with SIFs of variable surface coverage. Detection angle is noted in parentheses. Error bars are calculated from five separate samples.

the MEF effect diminishes. Moreover, p-polarized emission preferentially couples to silver overlayer first and to the copper thin films and is emitted at the SPCF angle from the back of the copper thin films, as evident from the measured p/s ratio (Fig. 4) and the free-space emission and SPCF intensities (Fig. 5).

4. Conclusions

Further enhancements of surface plasmon coupled fluorescence (SPCF) and free-space emission from copper thin films using silver islands as an overlayer is demonstrated. Silver islands were deposited onto copper films using a simple wet chemical technique for 20–60 s. This procedure yielded a silver overlayer with features ranging from random particles for short deposition times (20 s) to thin films (60 s) for longer deposition times as confirmed by SEM. Theoretical Fresnel calculations have shown that the angle of minimum reflectivity is predicted to shift from 60° for copper alone to smaller angles with a silver overlayer. The experimental verification of these theoretical predictions was undertaken by measuring the SPCF and free-space emission from Rhodamine B spin-coated onto silvered copper thin films, although fluorophores over much of the visible spectral range are expected to couple. The silver islands deposited onto 40 nm copper thin films for 50 s resulted in the largest enhancements of SPCF and free-space emission. The SPCF intensity from silvered copper thin films occurred at angles smaller than those from copper thin films alone and was found to be highly polarized. The procedure for the preparation of silvered copper thin films described here can be applied to other metal nanoparticle-thin film combinations and offers an opportunity to enhance the sensitivity of SPCF-based bioassays.

Acknowledgements

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