

## The Apparent Optical Indices of Spongy Nanoporous Gold

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### Introduction

Very thin spongy nanoporous gold films have a unique nanostructure and hence unusual properties. Our interest in these materials is also due to their wide range of potential applications [1,2]. An optical study for such nanostructured films is of fundamental interest for understanding how light interacts with such a spongy nanoporous structure. In general the gold either percolates or is very closely packed. Thus surface plasmons, and surface plasmon resonant effects, are expected to play a key role given the large surface area of metal and the metal backbone of the nanostructure. The topological complexity of the nano-void network is also expected to be a major influence. The optical response has, for a metal system, quite unusual dispersion relations for the effective complex refractive index components  $n^*$ ,  $k^*$ . Once these are better understood, new optical engineering possibilities arise.

We are not aware of any optical studies for spongy metal film nanostructures apart from a brief preliminary report of our own on one such film [3] whose nanostructure was different to the spongy nanoporous films presented here. We check the internal consistency and physical acceptability of the results with a Kramers-Kronig analysis of the spectrum of  $n^*$ ,  $k^*$  values, because of their unusual spectral character.

### Experiment

Alloy films of  $\text{AuAl}_2$  were prepared by co-depositing the elements using high vacuum dc magnetron sputtering onto glass substrates. The sputtering targets of Au and Al were 99.999% pure discs (50mm diameter), placed 150 mm away from the substrate. The base pressure was better than  $\sim 10^{-6}$  Torr, while sputtering was carried out in the presence of flowing Ar, at a pressure of 3 mTorr. To ensure good homogeneity and crystallinity, a 400°C substrate temperature was used during deposition. An atomic-force microscope (AFM) operating in tapping mode was used to determine the thickness of the films. Field emission scanning electron microscopy (FEGSEM) was used to study the nanostructure of the films. Figure (1) shows an image of a 20 nm thick spongy nanoporous gold film on a glass substrate.

The optical properties are measured using both ellipsometric and spectrophotometric techniques. Specular transmittance and reflectance ( $T$ ,  $R$ ) at normal incidence and  $T$  at 65° was measured in the range 300-800nm using a Cary 5E UV-VIS-NIR spectrophotometer. A Jobin-Yvon UVISEL, spectroscopic phase modulated ellipsometer is used in the same range. The spectroscopic scans were performed at 0° and 65° angles of incidence with respect to the surface normal, with 5nm wavelength intervals. Prior to spectroscopic scans on the ellipsometer the back surface of the glass

Topic area: CMMSP

substrate was covered with black tape to eliminate any back-surface reflection entering the detector because the 20nm spongy nanoporous gold layer is not opaque

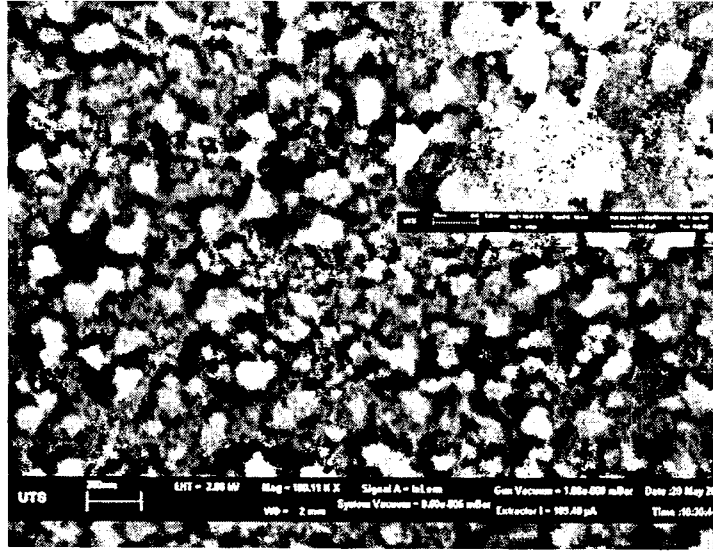


Figure 1: SEM image of the 20nm spongy nanoporous gold film taken at magnification X100000 while the inset image is at X188000.

## Results and Discussion

One spectrophotometric T scan of the sample at angle 65° is shown in Figure (2). Inset graphs show the ellipsometric  $\psi$  and  $\Delta$  results at the same angle of incidence.

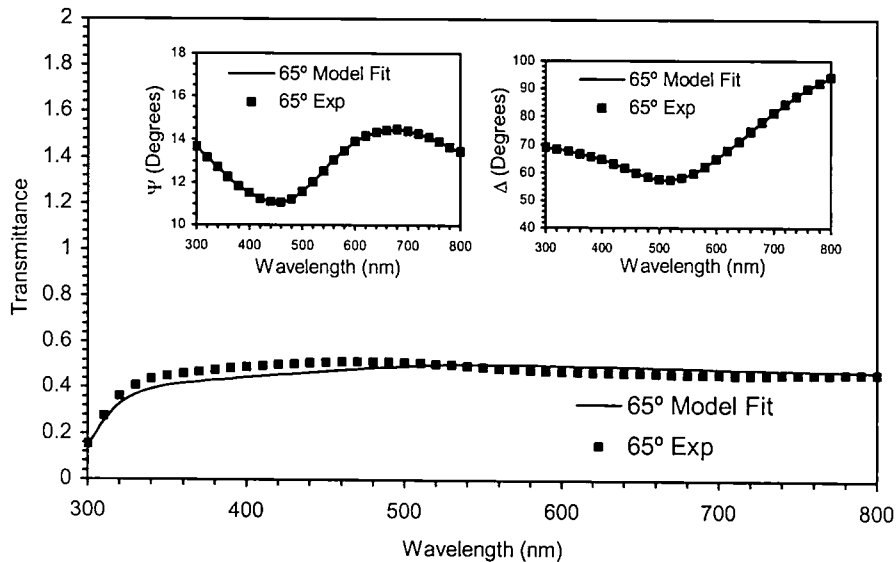


Figure 2: Main plot is spectrophotometric transmittance. Inset plots are ellipsometric data  $\psi$  and  $\Delta$  (All data was obtained at 65° incidence angle for a 20nm spongy nanoporous gold film on glass.

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Starting with accurately determined average film thickness using AFM we proceeded to determine the best fit complex indices that describe the data. In these procedures a “start” guess is needed for the unknown layer and we start with bulk gold data from Palik [4]. The fitting parameters are thus the apparent real part of refractive index ( $n^*$ ) and apparent extinction coefficient ( $k^*$ ), of the uniform layer that is optically equivalent to the spongy nanoporous layer at normal incidence and at  $65^\circ$ . Using the modelling software the spectrophotometer results (T) for the 20 nm spongy nanoporous film at angle  $65^\circ$  were fitted together with ellipsometric  $\psi$  and  $\Delta$  at the same angle. As can be seen in Figure (2) the least squares fitting were excellent for the whole wavelength range with a very small mean square error (MSE)[5]. Figure (3) shows the optical constants  $n^*$  and  $k^*$  as a function of wavelength and angle of incidence ( $65^\circ$ ). It is very clear that changing of incidence angle has a greater

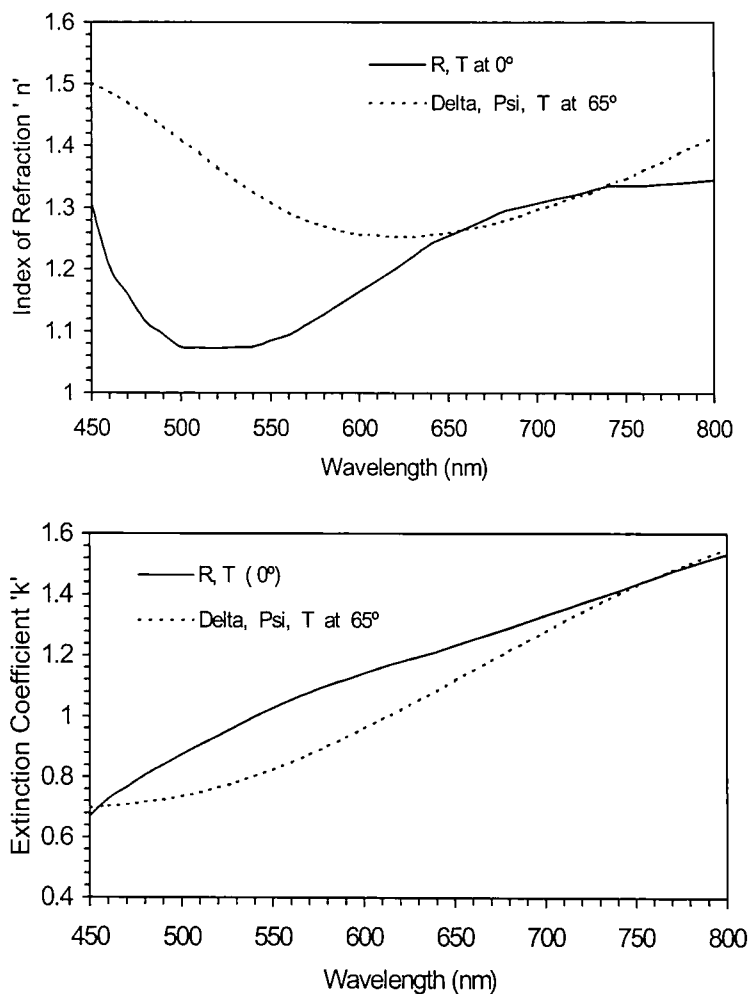


Figure 3: Optical constants ( $n^*$ ) and ( $k^*$ ) as a function of wavelength and angle of incidence for a 20nm spongy nanoporous gold film on a glass substrate obtained from the fit of ellipsometric data ( $\Delta$ ,  $\Psi$ ) combined with spectroscopic transmittance at  $65^\circ$  (dotted line) and transmittance and reflectance at  $0^\circ$  (solid line).

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effect on the real part of refractive index ( $n^*$ ) than on the extinction coefficient ( $k^*$ ). At longer wavelengths (using spectrophotometry only)  $k^*$  at  $0^\circ$  and  $65^\circ$  match, but  $n^*$  does not. The results verify what we predicted in earlier work for different metal nanostructures, namely that equivalent layer optical constants would change as angles of incidence varied [3] due to surface plasmon coupling across the layer. To determine if the fit parameters are physical the results must be Kramers-Kronig consistent. KK analysis shows they are physical (details appear elsewhere [6]).

### **Conclusion**

Very thin spongy nanoporous gold films on glass substrates were produced for the first time and the optical properties were explored. Variable angle ellipsometer and spectroscopic methods were used to study optical properties in order to extract optical constants at two different angles of incidence. We found changes in the angle of incidence have a strong impact on the refractive index ( $n^*$ ) but not on the extinction coefficient ( $k^*$ )

Spongy nanoporous gold films exhibit unique optical constant dispersion relations for a metal based system. For example they are completely different from those of typical 20nm gold films we have deposited using the same sputtering system. The effective optical constants as a function of wavelength, which are physically acceptable from a dispersion viewpoint, are neither metal- nor insulator-like. This is in effect a quite new class of optical material.

### **References**

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