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Nanoscale coatings of $AuAl_x$ and $PtAl_x$ and their mesoporous elemental derivatives

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Abstract

A method to produce nanoscale films of $AuAl_x$ and $PtAl_x$, and their mesoporous elemental derivatives is described, and the morphology and optical properties of these coatings explored. The color of the $AuAl_x$ film is bright purple, in agreement with *ab initio* calculations and experimental observations for the compound $AuAl_2$, but becomes black after de-alloying with NaOH. The film of $PtAl_x$ is silver-grey and changes to grey after being converted to mesoporous Pt by de-alloying. Both mesoporous coatings exhibit a very rough surface, with pores of between 2 and 20 nm in diameter, and display a significantly more absorptive optical characteristic compared to their ordinary elemental counterparts.

Keywords: mesoporous gold, platinum, optical properties

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1. Introduction

Most metallic elements will rapidly oxidize, usually pyrophorically, if they are exposed to air while in a mesoporous or nano-particulate form. The noble metals Au and Pt are the sole exceptions to this rule. This has led to much research on nano-particulate Au and Pt, with interest in the former being primarily focused on its surface chemistry and plasmon resonance with visible light, and on the catalytic efficacy of the latter. However, there has been less work on mesoporous sponges, which can be considered to be the geometric inversion of nano-particle aggregations, and which can be crudely modeled as a dispersion of overlapping spherical voids within a continuous metallic matrix [1,2]. Some schemes to prepare mesoporous metallic materials have been mentioned in the literature. These include de-alloying of suitable alloys [1-5], electrodeposition [6] and, recently, precipitation onto an organic template [7,8]. Among other reasons, mesoporous metals are of interest because of their catalytic properties and their double layer capacitance, which suggest possible uses as electrodes in fuel cells [8] or as electrodes in medical systems requiring functional implants and sensors [2,9]. However, our focus in the present work is on the optical characteristics of these materials. Production of mesoporous Au from bulk material has been previously described [1,2,4] but this is an inherently expensive process due to the quantity of the precious metal required and, in many potential applications, a nanoscale coating of mesoporous metal would be sufficient. Here we describe the production of such coatings of Au and Pt by the de-alloying of intermetallic precursor films.

The aluminide compounds $AuAl_2$ and $PtAl_2$ are suitable precursors for this purpose because they are susceptible to attack by alkali and may be de-alloyed in a manner analogous to that used in the preparation of Raney nickel catalysts [1,4]. However, these compounds are also interesting in their own right. They have the cF_{12} (CaF_2) structure and, like most other intermetallic compounds with this lattice, are highly colored. $AuAl_2$ is bright purple whereas $PtAl_2$ is yellow. Both compounds have been previously investigated for application in jewelry on account of their content of precious metals [10-12], while $PtAl_2$ is a useful barrier coating for jet engine turbine blades [13] and $AuAl_2$ has potentially attractive tribological [14] and decorative properties [15].

2. Experimental

Alloy films of $AuAl_x$ and $PtAl_x$ ($x \approx 2$) were prepared by physical vapor deposition (PVD), by co-depositing the elements using high vacuum dc magnetron sputtering onto glass substrates. The sputtering targets of Au, Pt and Al were 99.999% pure discs of 50mm diameter placed 150 mm away from the substrate. The base pressure was better than ~1×10^{-4} Pa, while sputtering was carried out in presence of flowing Ar, at a pressure of 0.2 Pa, to ensure good homogeneity and crystallinity. The substrate was heated to 400°C during deposition in order to facilitate compound formation. The rates of evaporation of the elements were each separately calibrated in order to produce the desired stoichiometry. Finally, very thin mesoporous films of gold or platinum were prepared by de-alloying the intermetallic coatings in 0.5M NaOH solution to produce materials designated here as Au_{meso} or Pt_{meso}. Ordinary PVD deposits of Au and Pt were also produced for comparative purposes, and are designated Au_{PVD} and Pt_{PVD}. The quantity of precious metal used was equivalent to a layer of 20 nm thickness in all cases. It was found that the Au_{meso} did not adhere well to the glass after de-alloying. The problem could be solved either by prior bombardment of the glass surface with high energy argon ions, or by first depositing a binding layer of chromium. Only results for the former case are shown here because application of a Cr underlayer significantly increased reflectivity and opacity of the coatings. However, the presence of the Cr did not have any discernible effect on the morphology of the gold sponge, nor was there any evidence that the Cr had migrated into the overlying Au layer. There were no problems with regard to the adherence of the Pt_{meso}. The specular reflectance and transmittance of the films were measured at normal incidence in a Cary 5E UV-VIS-NIR spectrophotometer.

The optical properties of these films, both as compounds and as mesoporous sponges, are of particular interest to the authors, and a capability to predict them by computation would allow a more rapid exploration of these materials. We have shown elsewhere [16] that the optical properties of Au_{meso} can be modeled empirically, but an *ab initio* solution of that system has not yet been achieved due to its geometric complexity. Some qualitative attempts [*e.g.* 17] have been made to calculate the visible spectra of $AuAl_2$ and $PtAl_2$, but here we show, possibly for the first time, how the properties of $AuAl_2$ can be calculated *ab initio* with reasonable success. The CASTEP code [18] was used in this calculation. The total energy is calculated within the framework of the local-density approximation (LDA) for the exchange-correlation energy. An energy cutoff of 700 eV was used for the expansion of the wave functions where a single point sampling of the Brillouin zone produced converged results in the Fourier space. The interactions between the ionic cores and the electrons are described by norm-conserving pseudopotentials [19], and the electronic wave-function is represented using a plane-wave basis set. The pseudo-wave functions, the smooth part of the charge density, and the potential are represented on a fast-Fourier transforms (FFT) grid of 27x27x27. These minimum FFT grids applied to the exchange-correlation potential are sufficient for the cutoff energies. Twenty sampling *k*-points in the irreducible wedge of the Brillouin zone were used, and were generated using the Monkhorst-Pack scheme [20] with parameters 7x7x7.

Geometry optimization calculations of $AuAl_2$ were considered to be converged when the maximum force on an atom was below 0.01 eV $Å^{-1}$. Optical properties have been calculated by performing a single point energy calculation to evaluate the self-consistent charge density, which allows the construction of the fixed Hamiltonian. The Kohn-Sham eigenvalues for many more *k*-points (for the Brillouin zone integration) and many more unoccupied states are then determined for this fixed Hamiltonian. The matrix elements for transitions between the occupied and unoccupied states are evaluated at this stage.

3. Results

Morphology of de-alloyed coatings

The de-alloyed sponges are very rough and porous at the nanoscale (Fig.1) . The pores in the Au_{meso} coatings range in diameter from 6 to 20 nm, with a mean of about 11 nm. Given that they were produced by dissolution of the Al, they must therefore form a generally continuous network. The pores in the Pt_{meso} were significantly smaller, being spread from 2 to 12 nm, with a peak at about 6 nm.

Reflectance spectra of $AuAl_x$ and $PtAl_x$ and their mesoporous derivatives

The spectrum of the $AuAl_x$ coating shows a minimum in reflectivity at 530 nm and a local maximum at 440 nm (Fig. 2) and it is these features that gives it its pronounced purple color. The spectra of Au_{PVD} and Au_{meso} are also shown in Fig. 2. After de-alloying, the gold loses its high reflectivity, and becomes markedly absorptive across the spectrum. The color of Au_{meso} is black rather than the yellow of Au_{PVD}. However, the Au_{PVD} is neither as shiny nor as yellow as polished, bulk gold (also shown), due probably to the surface roughness of the former. It was noted that while freshly de-alloyed mesoporous gold was black in color, thick deposits of it gradually changed to yellow with time, with the transformation complete in dry samples in less than ten minutes. From this it can be deduced that the surface shown in Fig.1a is probably produced by coalescence and sintering of a more open, metastable structure originally present on the wet specimen.

The reflection spectrum of Pt_{meso} is qualitatively similar to that of Au_{meso}, showing a flat spectral response. However, the reflectivity of the Pt_{PVD} is low, indicating that, under the conditions of PVD used here, a smooth and shiny coating of Pt was not achieved. The $PtAl_x$ coating had a silver-grey color. The lack of a yellow hue indicates that the compound $PtAl_2$ did not form.

Efficacy of ab initio calculation

The calculated reflectance spectrum of $AuAl_2$ is compared in Fig. 2(c) to measured data for the bulk phase produced by button arc melting [2], and for the $AuAl_2$ coating produced in the present work. The calculated data have been normalized to give a reflectivity of 45% at 330 nm. It is evident that while the curves are very similar in form, the calculated minimum is blue-shifted by 60 nm. The reason for the discrepancy may lie in some undiscovered inefficiency in the computational process. However, it is also possible that it is the result of the fact that the position of the minimum in the reflectance spectrum of $AuAl_2$ is significantly influenced by both dislocation and vacancy density [21]. It has been reported that samples of $AuAl_2$ may be sub-stoichiometric in Al, with a composition corresponding to Au_6Al_{11}, and a corresponding high density of constitutional vacancies [12]. Lattice defects were not taken into account in our calculation.

4. Discussion

The optical properties of these comparatively simple systems exhibit marked plasticity, and coatings with specular, absorptive or coloured responses can be readily prepared. Applications in the areas of solar glazing and other specialized coatings on transparent surfaces are of obvious relevance. However, the porosity and high surface area (up to 20 m^2/g) of mesoporous gold and platinum suggest some additional applications as well. For example, they have the potential to be exploited as electrodes on which to develop electrochemical double layer capacitance. Some details on this possibility, in so far as it applies to Au, have been presented elsewhere [2]. In broad summary, such coatings can manifest a capacitance of 2 mF/cm^2, a figure which is about a thousand times greater than the 50 to 100 $\mu F/cm^2$ exhibited by planar gold surfaces. While storage of electrical energy in consumer devices is not a likely application for these materials, they may have possible applications in capacitive bio-sensors and similar specialized items.

5. Conclusions

We have shown here that nanoscale, mesoporous coatings of Au and Pt can be prepared from intermetallic precursors produced by physical vapor deposition. The mesoporous materials are characterized by pores in the size range 2 to 20 nm, with those of the Pt being significantly smaller than those of the Au, as prepared here. The optical properties of the mesoporous materials are very different from that of ordinary PVD coatings of the elements, and exhibit a remarkably flat and absorptive spectral response. The method used produced near stoichiometric $AuAl_2$, the optical properties of which we were able to model, *ab initio*, with reasonable success.

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LIST OF FIGURE CAPTIONS

Fig. 1. Morphology of mesoporous metal films, (a) Au_{meso}, (b) Pt_{meso}, (c) distribution of pore sizes.

Fig. 2. Reflectance spectra of coatings, (a) $AuAl_2$, Au_{meso} on Ar-ion etched glass, Au_{PVD} and bulk Au, (b) $PtAl_x$, Pt_{meso} and Pt_{PVD}, (c) calculated and measured reflectance spectra of $AuAl_2$.

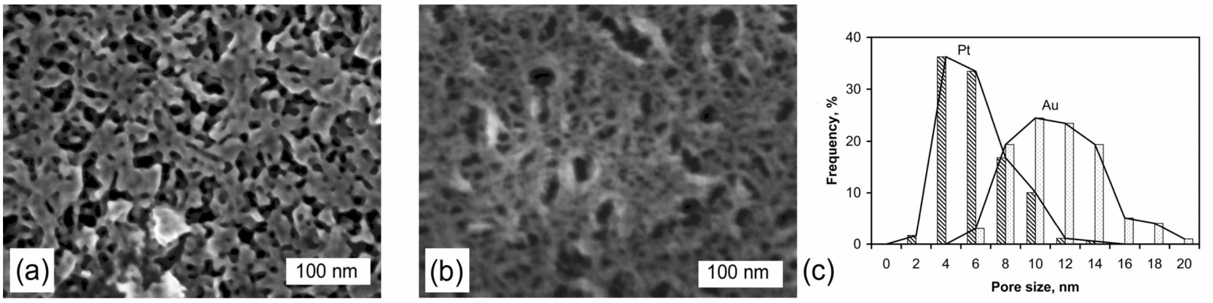

Fig. 1.

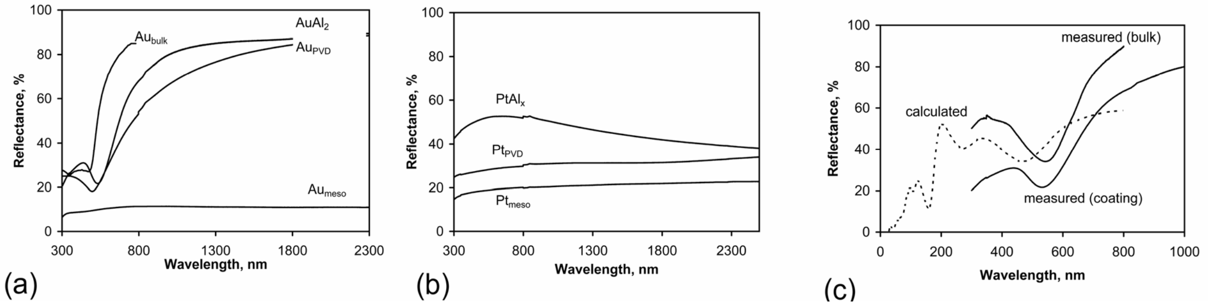

Fig. 2.