APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 9, 83-88 (1995)

The Structure of Very Thin Gold Layers Produced by Metalorganic Chemical Vapour Deposition

D. W. Allen and J. Haigh
Division of Chemistry, School of Science, Sheffield Hallam University, Sheffield S1 1WB, UK

Gold layers have been deposited from methyl(triethylphosphine)gold(I) by metalorganic chemical vapour deposition (MOCVD) and their structure and composition examined. At two deposition temperatures the layers have an underlying structure which is fine-grained in the case of the 500 °C layer and therefore of interest for thin-layer device structures. Impurity levels are low in this layer.

Keywords: MOCVD; metalorganic deposition; metal layer; gold

INTRODUCTION

Metal layers of thickness less than 500 nm are attracting attention because of their electrical, optical and magnetic properties. They are usually needed in the form of stacks, where adjacent layers may be required to have very different physical properties. A prime requirement, particularly for ultrathin (<100 nm) layers, is that they be exceptionally flat, so that for example the scattering of electrical carriers or photons moving through the layers is minimized. Layers deposited by metal vacuum evaporation or sputtering have been widely used, but surprisingly there appears to have been little investigation of the flatness of these layers (but see Ref. 1), on the scale where the irregularities have dimensions less than light wavelengths.

Metalorganic chemical vapour deposition (MOCVD) potentially offers a method for forming layer stacks which would be complementary to more established methods. Many metalorganic or organometallic (MO) compounds when pyrolysed yield encouragingly pure deposits of the metal, and these deposits often form as coherent layers. Because the efficiency of the MOCVD process does not depend on the vapour pressures of elemental metals, which do of course vary widely, the possibility exists of combining both refractory and volatile metals in one stack. Further, since MOCVD operates in a controlled gas atmosphere, which may be made highly reducing, factors such as the residual contents of the atmospheric gases oxygen and nitrogen (which are often found in transition-metal layers) might prove to be more easily controllable than in the standard methods. MOCVD used to generate thin metal layers is as yet largely unexplored, but can potentially draw upon the extensive experience accumulated in metalorganic vapour-phase epitaxy (MOVPE) of compound semiconductors, two results of the development of which have been to provide equipment design knowledge and to make reliably pure metalorganic compounds commercially available.

One metal for which the MOCVD method might prove valuable is gold, which is widely used in ultrathin layer form for metallizing semiconductors, in combination with highly refractory metals such as tungsten and titanium. Although gold metal is relatively volatile, unreactive to air, and hence easy to deposit by conventional vacuum evaporation, its ubiquity in technology in combination with other metals means that any practical MOCVD method for depositing the refractory metals would thus also have to be able to deposit gold. The investigation of MOCVD processes for gold layer formation is therefore of value.

As recently extensively reviewed by Puddephatt,[2] published work on the formation of gold layers from organometallics has concentrated on the dialkylgold(III) β-diketonates, although less has been done on mechanisms of deposition with these species. As work cited in Ref. 2 shows, the rather simple chemistry of the thermolysis of another group of gold organometallics, of formula AuRL and AuR_3L (where R is usually Me, and L is a trialkylphosphine ligand), makes them also attractive as layer precursors. Several of the species in this group have been used for laser-induced layer deposition.[3,4]

CCC 0268-2605/95/010083-06

Received 19 May 1994
Accepted 3 October 1994

Thus Davidson and co-workers[4] have deposited gold from methyl(trimethylphosphine)gold(I) on to gallium arsenide using laser pyrolysis, and have shown it to have an electrical resistivity as low as three times the value for bulk gold, indicating an encouraging degree of purity. Banaszak and co-workers[5] have used ethyl(trimethylphosphine)gold(I) to deposit gold in an ultrahigh-vacuum (UHV) system at room temperature.

Once an MOCVD precursor is available, the production of very thin layers requires an investigation of the balance between nucleation and growth processes in the deposition. The metal atoms assembling to form the layer have some variable degree of mobility on the surface, and in any deposition process this movement can lead to the aggregation of the atoms into nuclei. The greater the activational barrier to the formation of these nuclei, the fewer in number they will be at any time and the further atoms will have to migrate to find them. (This migration is also, of course, an activated process.) The production of a flat layer requires the mean distance between nuclei to be less than the layer thickness aimed for. In the extreme, where nucleation is possible at all points and migration distance is zero, the greatest flatness results. This condition is best approached in epitaxial deposition. The balance between rates of arrival of atoms or molecular moieties at the surface and their migration to nuclei can in principle be varied by changing the thermodynamic overpotential for the deposition reaction, although it is difficult to predict the exact form of the overpotential dependence that will be observed. In practice this variation can be achieved by controlling the temperature of the substrate and the vapour pressure of the metalorganic compound in the gas stream. Since rates of activated processes change rapidly with temperature, experimenting with this variable is likely to be the most productive approach.

One problem with the study of thin layers is that their morphology is often strongly influenced by the nature of the surface upon which they nucleate. Substrates of uniform and controllable surface are required. The Group III–V semiconductors provide such surfaces, and for this reason the present work was carried out using the (100) surfaces of polished gallium arsenide and silica, for which reliable cleaning and polishing procedures, known to give reproducible results in epitaxial growth, are available.

DEPOSITION OF GOLD BY PYROLYSIS OF METHYL(TRIETHYLPHOSPHINE)GOLD(I)

The alkyl phosphine (PR_3) complexes of gold(I) and gold(III) alkyls are stable to temperatures often approaching 100 °C, and their covalent

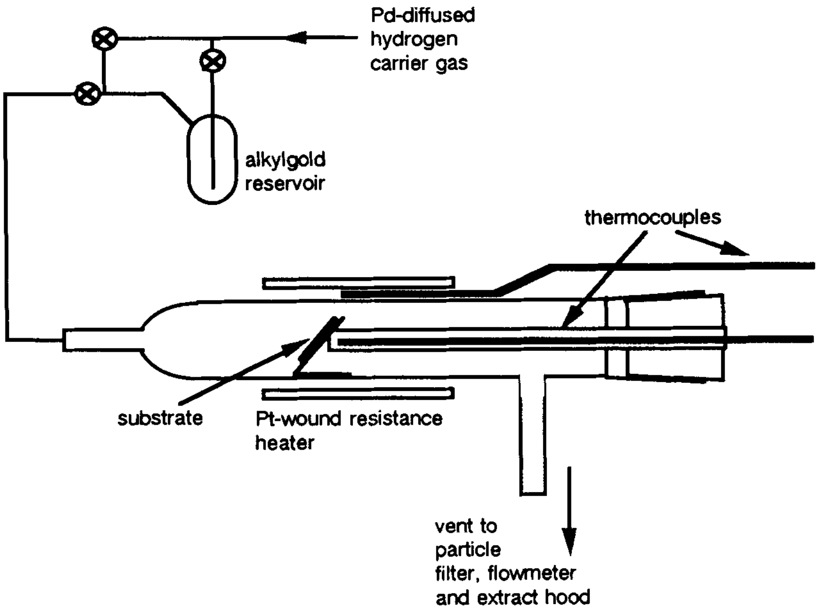


Figure 1 Schematic diagram of the deposition apparatus.

nature gives them appreciable volatility. For the present work the species $CH_3Au \cdot P(C_2H_5)_3$ was chosen. It was synthesized by standard methods[6,7] and purified by recrystallization, melting point 58–60 °C. Decomposition is stated[6] to begin at the melting point. The vapour pressure of the complex, which would make possible the prediction of the deposition rate assuming complete decomposition, is not known with any certainty.

Group III–V semiconductor substrates, prepared by the manufacturer by sawing and chemomechanical polishing, were cleaved into 6 mm × 6 mm squares and cleaned with acetone by swabbing followed by ultrasonic immersion for 2 min. For comparison in some cases, silica substrates were used, cleaned in a similar way. The deposition apparatus is shown schematically in Fig. 1. The substrate was placed at an angle to the gas flow on a molybdenum sample holder in a rectangular-section silica tube of internal dimensions 10 mm × 10 mm, connected to a glass bubbler (a container allowing gas to be bubbled through a liquid metalorganic sample). The tube was heated by an electrical winding. A stream of hydrogen, purified by diffusion through palladium, was passed through the bubbler, which was held at 30 °C, then over the heated substrate in the tube, and finally to waste via a particle filter. All the components of the equipment were stainless steel, PTFE, silica or glass.

The deposited layers were examined using scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and optical microscopy. The X-ray photoelectron spectrophotometer was part of a Vacuum Generators Microlab, using aluminium Kα radiation to generate electrons from the sample, which were collected by a hemispherical analyser using an array of five channeltrons. Etching was carried out in the same vacuum chamber using an argon plasma at about 10^{-5} torr, for 6 min per etch. The SEM was performed on a JEOL 840A.

SCANNING ELECTRON MICROSCOPY (SEM)

To obtain clear microscopic images of the grain size, the layers were abraded before examination with a soft cotton bud. This served to remove or displace the grains as whole units, without scratching the substrate. In this way the granular structure was revealed clearly at the edges of the abrasion, and by observing at low angles the layer thickness could be estimated.

It was usually found, from the several samples examined, that in places the abrasion removed only an upper part of the layer, leaving a well-defined underlying layer adhering to the substrate which could then be imaged separately. This was true of both MOCVD and vacuum-evaporated material. Figure 2(a) shows that the underlying part of the layer deposited at 400 °C substrate temperature on GaAs has a structure composed of grains around 0.1 μm in diameter. Some large detached needle-like crystals are produced on top of the layer, indicating that homogeneous nucleation (formation of nuclei not in contact with the substrate surface) is occurring to some extent. Layers deposited under similar conditions on silica proved difficult to image over large enough areas because of their poor conductivity, but in those small areas where images could be obtained the structure was similar.

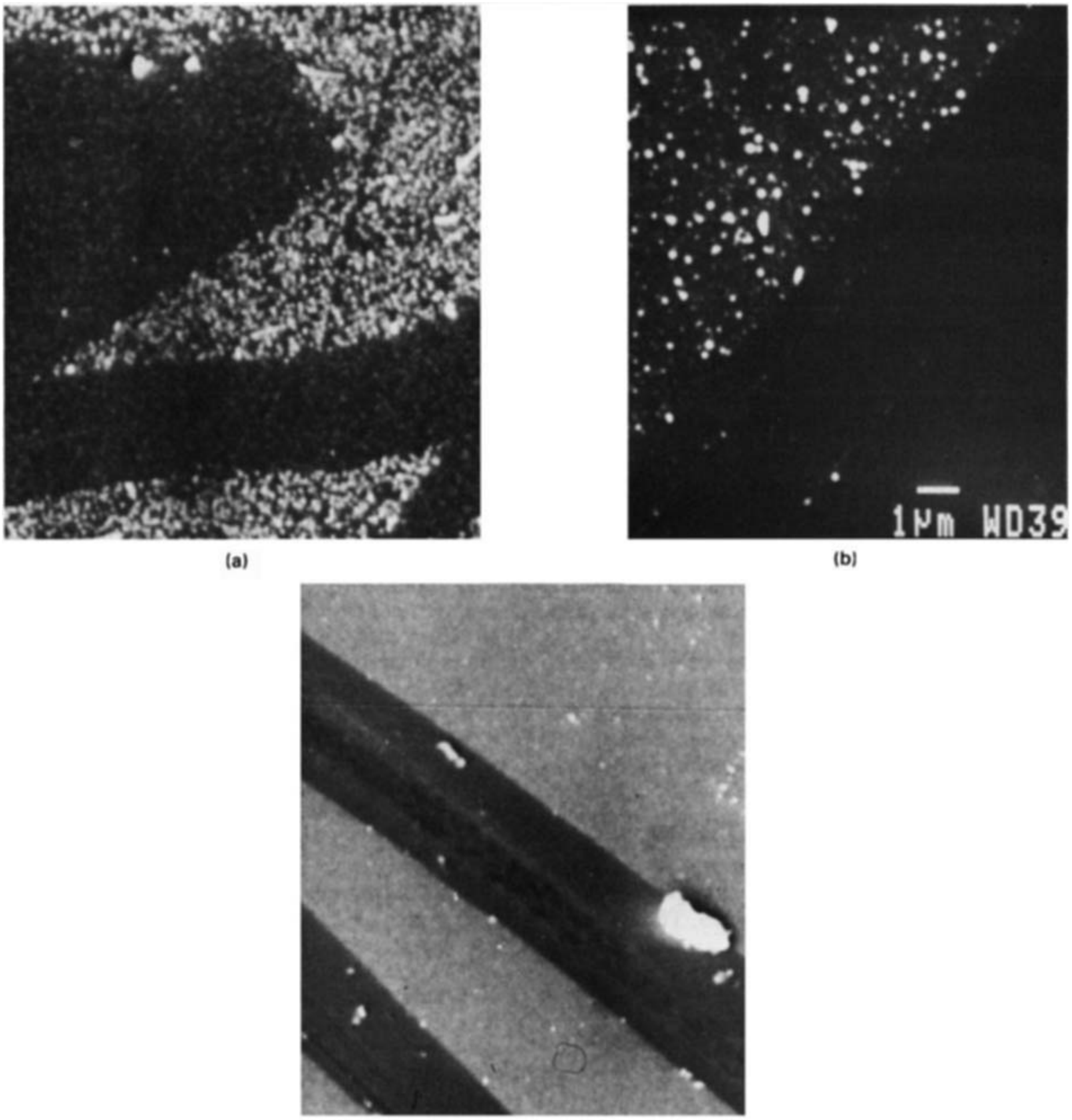
Layers deposited at 500 °C on GaAs and silica have a rather similar structure to those at 400 °C, but the underlying part is finer and not resolved into grains by the SEM (Fig. 2b). In the sample shown, both upper and underlying layers have been removed in the abraded regions.

A comparison is given with a vacuum-evaporated gold film on glass (Fig. 2c). The grain structure in both the upper and the underlying material is much finer than in the MOCVD layers.

An upper estimate of overall layer thickness of 0.5 μm is indicated for both MOCVD layers. It was not possible by imaging to determine the thickness of the underlying layer.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS determinations were made of peak intensities characteristic of carbon, oxygen, gallium and gold emitted by a sample deposited at 500 °C. The irradiating X-ray beam was broad enough to cover the entire sample so as to maximize the precision of peak intensity determination, but this precluded the possibility of separate examinations of the upper and underlying regions since no imaging was possible. After a determination made on the layer as-deposited, the sample was treated briefly in an argon plasma without removal from the vacuum, and then the intensities and peak positions were remeasured. Care was taken to return the sample to the same position and orientation in the beam after the plasma treatment. The plasma treatment was repeated. After the second treatment it was observed that the gold appearance of the layer had substantially disappeared.



(a)

(b)

(c)

Figure 2 (a) SEM image of an MOCVD gold layer deposited on GaAs at 400 °C. The dark band shows where material has been removed by abrasion. An underlying granular layer is observed. (b) SEM image of an MOCVD gold layer deposited on GaAs at 500 °C. In the abraded dark area all of the layer has been removed. The underlying part appears as an unresolved bright background between the overlying coarser crystals. (c) SEM image of a vacuum-evaporated gold layer on glass. Both upper and lower layers show an unresolved fine-grain structure. Magnifications in (a) and (c) are the same as in (b).

Table 1 XPS peak intensity as a function of stages of plasma treatment: sample deposited at 500 °C

	Intensity (counts sec^{-1})		
	C (285/284.5)[a]	O (532)[a]	Ga (1117)[a]
Surface	17 000	50 000	20 000
After first plasma treatment	9000	10 000	130 000
After second plasma treatment	2300	8000	130 000

[a] Peak position in eV is shown in parentheses.

Discussion of XPS results

The 500 °C sample layer was chosen for examination because its underlying component seemed to show the greater flatness. Table 1 shows the peak intensities (as counts per unit time) for emissions typical of the three elements carbon, oxygen and gallium. The gold emission peaks are shown separately in Fig. 3.

It can be seen that the count for gallium rose substantially after the first plasma treatment, remaining at the same level after the second treatment. (An identical rise, not detailed here, was observed in the arsenic peak.) At the same time there was a shift of about 0.5–1 eV to higher energy in the gold peaks and a large reduction in their intensities. The levels of carbon and oxygen also fell as a result of the plasma treatment.

The intensity of the gallium signal from the sample before plasma treatment is attributable to regions of the substrate which were shielded by the sample holder during deposition of the metal and therefore presented an uncovered GaAs surface. As a result of the plasma treatment a large part of the gold was removed from the sample, exposing more gallium arsenide, as shown by the concerted changes in the gold and the gallium signals. At the same time the carbon and oxygen levels fell, and the fact that they remain unchanged by the second etch suggests that this lower level may represent carbon and oxygen adsorbed on the original GaAs surface before deposition, or transferred to it during plasma treatment. A small shift in the carbon peak to lower energy (<0.5 eV) is observed after the second plasma exposure, which may support this suggestion. If so, it can be inferred that the carbon and oxygen levels observed on the original gold layer, being only two-fold or so higher than the levels after two plasma treatments, are also low and may arise from surface adsorption or adventitious intergrain trapping. The MO deposition process is conducted in the rigorous absence of oxygen, so that this element can in any case arise only as a result of air exposure. The peak position shift of the gold may be due either to removal of the carbon and oxygen, assuming them to be bound and capable of producing an energy shift in the emission of the original layer, or to diffusion of the gold into the substrate, which would generate a shift compared with the original layer. However, the large reduction in the gold signal compared with that in the carbon and oxygen signals makes it seem unlikely that adsorbed carbon and oxygen are present in sufficient amounts to account for the shift. In itself this reduction indicates that substantial amounts of gold have either been evaporated or driven into the substrate by the plasma—a rise in tem-

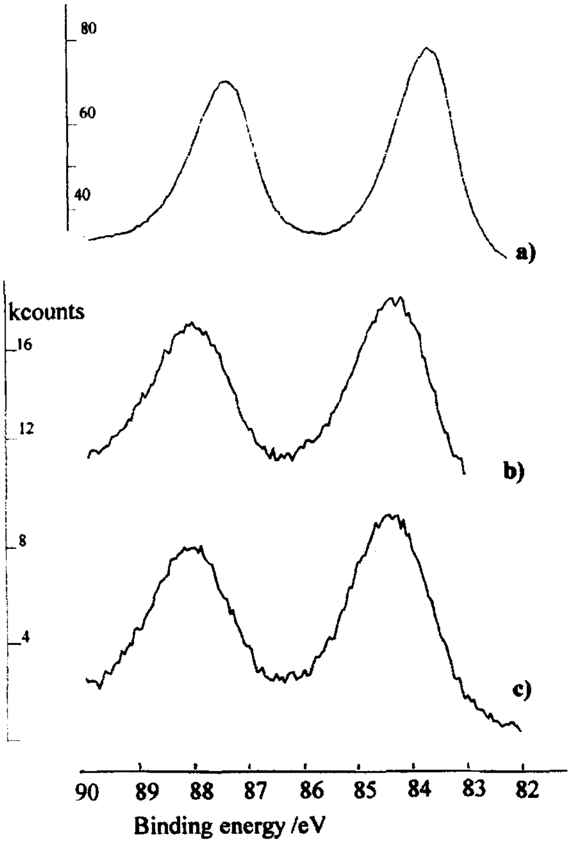


Figure 3 XPS traces characteristic of gold, obtained from an MOCVD gold layer deposited on GaAs: (a) untreated; (b) after one plasma treatment; (c) after two plasma treatments. Binding energies are shown as (irradiation energy – kinetic energy), where the irradiation energy is 1486.6 eV (Al K_{α}).

perature sufficient to bring about the former process would certainly allow the latter also.

CONCLUSIONS

We have observed conditions under which reasonably flat and impurity-free thin layers of gold may be deposited by MOCVD, although these are then overgrown by material of a coarser structure. These layers are candidates to be incorporated into structures of novel electrical properties.

Acknowledgements We thank Mr K Blake, Mr P Slingsby and Mr C Blomfield for technical assistance, and Mr K Schofield for preparing the gold complex. We are grateful to the Nuffield Foundation for financial support.

REFERENCES

1. J. Hwang and M. A. Dubson, *J. Appl. Phys.* **72**, 1852 (1992).
2. R. J. Puddephatt, *Polyhedron* **13**, 1233 (1994).
3. For example, M. Jubber, J. I. B. Wilson, J. L. Davidson, P. A. Fernie and P. John, *Appl. Phys. Lett.* **55**, 1477 (1989).
4. J. L. Davidson, P. John, D. K. Milne, P. G. Roberts, M. G. Jubber and J. I. B. Wilson, *Adv. Mater. Opt. Electron (UK)* **2**, 3 (1992).
5. M. M. Banaszak, P. F. Seidler, S. K. Kowalczyk and F. R. McFeely, *Appl. Phys. Lett.* **62**, 1475 (1993).
6. G. Calvin, G. E. Coates and P. S Dixon, *Chem. Ind. (London)* 1628 (1959).
7. G. E. Coates and C. Parkin, *J. Chem. Soc.* 3220 (1962).