

UV-induced decomposition and interrogation of novel metal-precursor films

J. A. Cairns, G. J. Berry, R. A. G. Gibson, A. G. Fitzgerald and Y. Fan

Division of Electronic Engineering and Physics, University of Dundee, Dundee, DD1 4HN, UK

I. P. Clark and S. M. Tavender

Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK

R. A. Moody

Central Microstructure Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, UK

Main contact email address j.a.cairns@dundee.ac.uk

Introduction

The production of metal films, whether it be for making solder joints or for interconnecting components, is central to the whole of the electronics industry^[1]. In all of these applications it is vital for the metal to exhibit strong adhesion to the substrate.

As a result of the rapid growth in demand for flat panel displays, there is much interest in depositing metal interconnects on to both glass and polymer substrates. Traditionally this is achieved by metal evaporation or sputtering. However there are problems: this is an expensive and time-consuming operation; and some metals, such as copper, exhibit poor adhesion to glass and to plastic.

We have devised an alternative approach. This involves using suitable organic liquid-phase precursors to deposit thin (typically 100nm) films onto the substrates. The films are then subjected to thermal decomposition, which results in their being converted to a porous oxide, within which are dispersed nano-sized metal particles. We have found that a particularly suitable oxide is zirconium oxide; and a preferred metal is palladium. The palladium behaves as a highly effective catalyst. Consequently when the films are immersed in an appropriate electroless plating bath (containing an aqueous solution of the salt of the metal to be deposited) highly structured, strongly adherent metal films (for example of copper, silver, nickel or gold) are produced. These films show excellent adhesion to a range of substrates, including the combination of copper on glass. In addition, they form strong solder bonds (as measured by quantitative shear force experiments). We believe that the adhesion is provided substantially by the porous zirconia, while the highly structured nature of the deposited metal provides the basis for the improved solderability. In contrast, copper deposited by thermal evaporation is less adherent to glass, and forms much weaker solder joints.

It is important to recognise that some of the most important applications involving metal films require them to be patterned—for example to make electrical interconnecting tracks. The printed circuit board is an obvious example of this. Traditionally such patterning is achieved by depositing a continuous film of the metal, and subjecting it to photolithography^[2]. This involves coating the metal with a layer of UV-sensitive photoresist, irradiating the photoresist through a photomask, selectively removing regions of the photoresist to expose the underlying metal, and finally etching away the exposed metal to leave the required pattern.

We have demonstrated that we also can use photolithography to produce metal patterns from the new class of metal films described above. However in the course of this work we observed that if the organic film, having been deposited on to the substrate and allowed to dry, is irradiated with deep UV (266nm) through a mask, the irradiated regions are rendered insoluble in the original solvent. The result is that a patterned film can be created, and this film in turn be plated to produce the desired metal pattern. A significant advantage of this process is that it avoids the production of the metal-containing effluent which is associated with traditional photolithography. An example of a pattern produced in this way is shown in Figure 1. In view of its important practical and environmental potential, it was considered important to understand more clearly the fundamental nature of this UV-induced process.

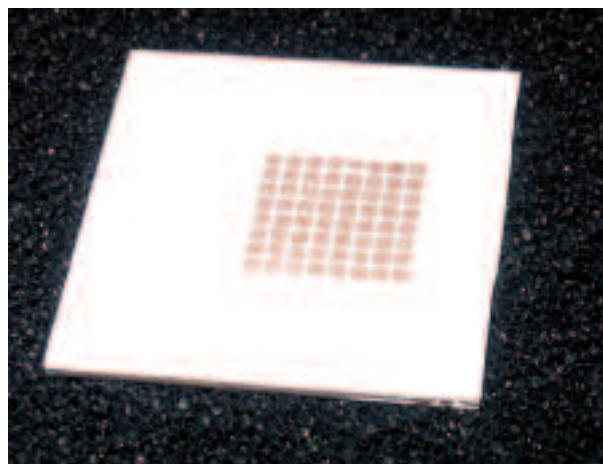


Figure 1. Pattern produced by direct UV irradiation of original film, followed by plating.

It was proposed that a significant insight into the mechanism would be obtained by subjecting the films to UV irradiation, while simultaneously using laser-induced Raman spectroscopy to follow the chemical changes dynamically. This resulted in our being granted access to the Nanosecond Laboratory for a two-week exploratory investigation.

Experiment

A pseudo pump-probe technique was employed, using a Nd:YAG pumped dye laser to provide the UV radiation, and a visible cw argon-ion laser to acquire the Raman spectra. It was reasoned that palladium acetate could act as a model compound, because it has a number of well-

documented absorption peaks^[3]. The broad electronic absorption (metal-ligand charge-transfer) centered around 360nm makes the third harmonic of the Nd:YAG an ideal pump source. This compound is also known to be stable to the 514nm argon ion line, thereby ensuring that it should resist degradation from the action of the probe laser. In addition, palladium acetate has at least three modes of coordination, which give rise to sharp $\nu(\text{Pd-O})$ vibrations in the solid phase over the 280 to 300 cm^{-1} region, thereby rendering Raman spectroscopy an ideal technique to monitor the transition from the organic to the metal/oxide state.

However, when the films were subjected to this process, it was found impossible to obtain a significant Raman signal. It was postulated that since the films were only of the order of 100nm in thickness, perhaps there was insufficient material present to generate a usable Raman signal. This was confirmed when trans-stilbene, a compound well known for its strong Raman response, was found to be incapable of yielding a usable Raman signal when deposited as a thin film of comparable thickness.

Consequently it became necessary to adopt an alternative strategy. A series of films was deposited on to quartz substrates, and subjected to UV/visible spectroscopy, in order to measure the UV wavelength at which maximum absorption occurred. This demonstrated that some of the organic precursors exhibited appreciable absorption, even in the I-line (365nm) region of the spectrum. This particular wavelength is used widely by the electronics industry for optical lithography. Accordingly, the films were exposed to a series of increasing doses at the Central Microstructure Facility at RAL, after which they were subjected to copper electroless plating. It was found that these irradiated films could be sufficiently decomposed, under the influence of the UV irradiation, to enable them to be plated subsequently with copper. This was an unexpected and highly satisfactory development.

Conclusions

Although it proved to be impossible to follow the decomposition of the films dynamically, as had been planned originally, it emerged that some very useful data was obtained, specifically that the decomposition can be induced by a wider range of wavelengths than previously had been envisaged.

References

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