

VUV synchrotron radiation processing of thin palladium acetate spin-on films for metallic surface patterning

Y. Zhang and M. Stuke

Max-Planck-Institut für biophysikalische Chemie, Postfach 2841, D-3400 Göttingen, Fed. Rep. of Germany

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Processing of thin palladium acetate spin-on films for the electroless copper plating has been carried out using UV and VUV synchrotron radiation. The mechanism of UV photodeposition of palladium from the thin palladium acetate film is studied.

1. Introduction

Thin palladium acetate films have been used for laser deposition (or prenucleation) of palladium lines, which can be used as a catalyst for electroless plating of other metals, notably Cu, to build up thicker conductors. This palladium deposition process was carried out using a CW argon ion laser at 514.5 nm for the first time in 1987 [1] then at 351 nm [2]. This visible-laser-induced deposition of palladium is a photothermal process since the Pd-acetate film precursor has no significant electronic absorption above 350 nm (see spectrum (a) in fig. 3). Powerful visible laser radiation has to be used to heat up the absorbing area of a substrate to initiate a deposition and therefore, this process cannot be carried out on a transparent substrate like quartz. Further, UV excimer laser (ArF at 193 nm, KrF at 248 nm or XeCl at 308 nm) was used for the same processing [3] since the film precursor has strong UV absorption at about 210 nm (see spectrum (a) in fig. 3). Although the processing with the UV excimer laser pulses was carried out on UV transparent substrate like quartz, it was still doubtful whether this process is *photolytic* or *photothermal* when the laser fluence threshold for prenucleation had been found for each UV excimer laser wavelength (see

Table 1
 Photodeposition of palladium from Pd-acetate spin-on films

Visible	Ar ⁺ (514.5 nm)	10 ⁵ W cm ⁻²	Gross et al. [1]
	Ar ⁺ (351 nm)	10 ⁴ W cm ⁻²	Cole et al. [2]
	XeF (351 nm)	> 200 mJ cm ⁻²	Esrom and Wahl [3]
UV	CeCl (308 nm)	> 80 mJ cm ⁻²	Esrom and Wahl [3]
	KrF (248 nm)	> 15 mJ cm ⁻²	
	ArF (193 nm)	> 10 mJ cm ⁻²	This work
	Synchrotron	< 0.6 mW cm ⁻²	
VUV	Synchrotron	< 25 mW cm ⁻²	This work

table 1). In order to clarify this, we studied the UV photochemistry of Pd-acetate spin-on film. The result of this study is in agreement with our successful experiment of deposition of palladium from Pd-acetate films using VUV synchrotron radiation with an average flux as low as 25 mW cm⁻². A comparison of the photodeposition of palladium from Pd-acetate spin-on films using different light sources is given in table 1.

2. Experiment

The palladium acetate ($\text{Pd}(\mu\text{-O}_2\text{CCH}_3)_2$) was spin-coated from a chloroform solution onto different substrates (Al_2O_3 ceramic, quartz and silicon wafer) to a thickness ranging from 0.02 to 1.5 μm , depending on solution concentration and spin speed. The thickness of the spin-on film was measured using a Sloan Dektak IIA stylus profilometer.

UV spectra of the palladium acetate film on a quartz substrate were recorded on a Shimadzu UV-160 spectrometer, which was also used to estimate the thickness of the thin film below 0.05 μm . IR spectra of the palladium acetate films on either a silicon wafer or an Al_2O_3 ceramic were recorded on a Nicolet 740 SX Fourier transform infrared spectrometer to monitor the chemical change inside the palladium acetate film exposed to UV laser light. A Balzers QMG 511 quadrupole mass spectrometer was used to detect desorbed species during the UV excimer laser irradiation of the Pd-acetate film under high vacuum.

The UV or VUV light source was taken either from a Lambda Physik EMG 500 excimer laser at

248 nm (KrF) or 193 nm (ArF), or from the synchrotron radiation provided by the electron storage ring (BESSY) in Berlin, which, through a Wadsworth monochromator without being dispersed (at the zeroth order of the grating), gives a 40–300 nm VUV beam of an average flux of 5×10^{15} photons $\text{s}^{-1} \text{cm}^{-2}$ at the focussed spot of $1.3 \times 1 \text{mm}^2$. Different wavelength ranges of the synchrotron radiation can be obtained using different windows, that is, 40–300 nm (without any window), 110–300 nm (with a LiF window) and 180–300 nm (with a quartz window). No difference in the processing was found in the different wavelength ranges.

The palladium deposit, after the substrate was washed in chloroform, was used for electroless plating of copper to check if enough Pd had been formed on the substrate surface.

3. Spectrometric study of chemical changes

At a low fluence level, namely 4mJ cm^{-2} , no palladium deposition could be induced from the palladium acetate spin-on film even after about

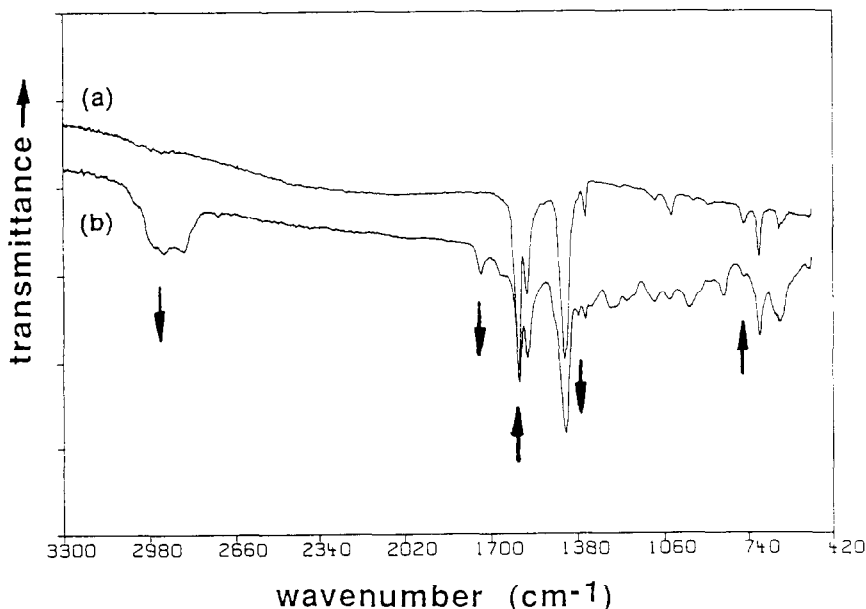


Fig. 1. FT-IR spectra ($420\text{--}3300 \text{cm}^{-1}$) of the palladium acetate film before (a) and after (b) exposure to about thirty thousand shots of 248 nm laser pulses at a low fluence level (4mJ cm^{-2}).

Table 2
Assignment of some changes of the IR spectral features in fig. 1

Wavenumber (cm ⁻¹)	Vibration	Change	Meaning
2950–2800	CH stretching of CH ₃	Increase	C–O bonds break
1726	C=O stretching of ester	Appear	Pd–O bonds break
1596	C=O stretching of carboxylate	Decrease	Pd–O, C–O bonds break
1370	CH ₃ –O deformation	Increase	C–O bonds break
765	C=O scissoring of carboxylate	Decrease	Pd–O, C–O bonds break

thirty thousand shots of UV excimer laser pulses at 248 nm or 193 nm. However, the chemical change in the film precursor after the irradiation can clearly be seen in the IR spectra shown in fig. 1, where some changes of the spectral features (see arrows) are assigned [4] and summarized in table

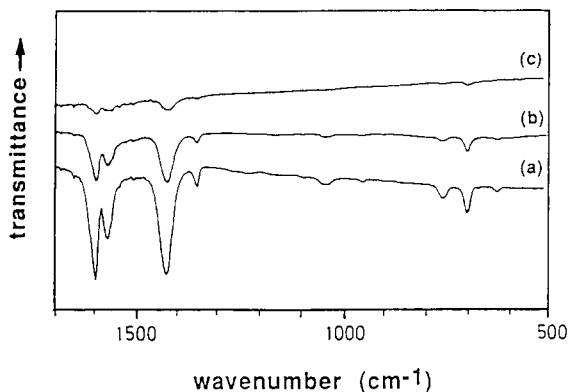


Fig. 2. FT-IR spectra (500–1700 cm⁻¹) of the palladium acetate film before (a) and after exposure to four shots (b) and to thirty shots (c) of 248 nm laser pulses with 12 mJ cm⁻².

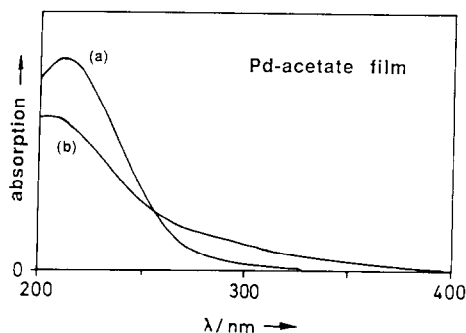


Fig. 3. UV spectra of the palladium acetate film before (a) and after (b) exposure to about thirty thousand shots of 248 nm laser pulses at a low fluence level (4 mJ cm⁻²).

2, which indicates that the palladium acetate film precursors have been dissociated by the UV laser light at 248 or 193 nm without seeing any film damage. The chemical changes under UV light are rather different from those under ion beam irradiation [5].

If the UV laser fluence was increased to above the prenucleation fluence threshold, the film was damaged and the palladium deposit appeared, which could be used for the copper plating. In this case, the spectral change in the IR spectra in fig. 2 behaves completely differently from that in fig. 1. Here, the monotonous decrease in all the spectral features indicates that all the molecular photofrag-

Table 3
Ion signals detected due to desorbed photoproducts^{a)}

Ions	m/e				
	59	44	43	27	15
O ₂ CCH ₃ ⁺					
CO ₂ ⁺					
OCCH ₃ ⁺					
CCH ₃ ⁺					
CH ₃ ⁺					

^{a)} The base pressure is 10⁻⁸ mbar.

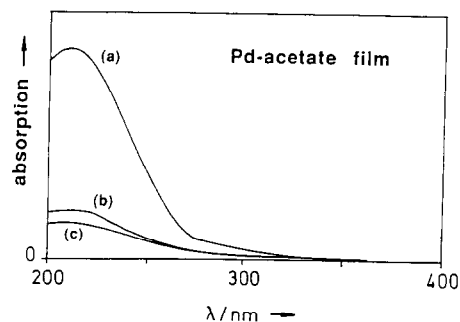


Fig. 4. UV spectra of the palladium acetate film before (a) and after exposure to four shots (b) and to thirty shots (c) of 248 nm laser pulses with 12 mJ cm⁻².

ments have been desorbed at a high laser fluence level, leading to the deposition of pure palladium. Actually, we measured the gas background by mass spectroscopy during the Pd-acetate film being exposed to KrF laser radiation above the fluence threshold for pre-nucleation and detected the desorbed photoproducts, as given in table 3. Our results in table 3 are somewhat different from those under ion-beam irradiation [6] but looks more reasonable. CO_2 seems to be a main desorbed species and no Pd-containing ions at $m/e > 100$ were detected. Although the smaller mass ions like CCH_3^+ and CH_3^+ may also be due to further fragmentation of the larger mass ones, we can conclude from table 3 that the Pd-acetate film precursor has been decomposed by the 248 nm laser pulse, with the ligand part and its photofragments desorbed and the palladium deposited, which is consistent with the results concluded from the IR spectra (fig. 2).

For a cross-check, the changes in the UV absorption spectra were also measured below and above the fluence threshold, as shown in figs. 3 and 4. Here again, the spectral change is shown in fig. 3 (below the fluence threshold) while the monotonous decrease is shown in fig. 4 (above the threshold). These results agree with those from the IR spectra.

4. Discussion

From the above observations it is now clear that below the fluence threshold, UV laser-induced *dissociation* of the palladium acetate film occurs but *no* deposition of palladium. This is similar to what has been found in the UV laser photoablation of organic polymers, namely the photolysis of the PMMA film before its photoablation, referred to as “incubation” [7]. Above the threshold, UV-laser-induced *desorption* of the ligand part photoproduct and its photofragments formed in the UV laser photolysis of the film precursors during a UV laser pulse results in *deposition* of palladium as seen. Since this fluence threshold for the photodesorption process may exist [8], therefore, it is not surprising to find a fluence threshold for the UV excimer laser deposi-

tion of palladium from Pd-acetate films. The pre-nucleation threshold depends on the absorption coefficient of the UV radiation and the thickness of the film. When the laser fluence is increased much higher than the pre-nucleation threshold, *photoablation* rather than the deposition occurs, where not only the ligand part and its photofragments but also the palladium deposit, maybe even the film precursor molecules before their decomposition, will be desorbed. This photoablation has been known as “negative process” and used for application as well [9].

As studied above, the fluence threshold for the photodeposition is due to minimum amount of energy needed for the photodesorption. The broad-band UV or VUV light may reduce the threshold, due to efficient coupling of the photon energy into the film through its broad-band absorption. Therefore, the VUV synchrotron radiation (40–300 nm) with an average flux as low as 25 mW cm^{-2} was used for the deposition of palladium from Pd-acetate spin-on films. Since the 180–300 nm synchrotron radiation (5×10^{14} photons $\text{s}^{-1} \text{ cm}^{-2}$) could be used to carry out the same processing on a *transparent* quartz substrate, no pyrolytic process should be involved. As shown in table 1, the fluence threshold is considerably reduced by using the synchrotron radiation. More recently, it was found that the broad-band UV Xe_2^* excimer lamp (166–178 nm) with a low flux of 125 mW cm^{-2} can also be used for the same processing [10]. All these results confirm our above study.

5. Conclusion

A processing of thin palladium acetate spin-on films for electroless copper plating can be carried out using UV and VUV synchrotron radiation of an average flux of 5×10^{15} photons $\text{s}^{-1} \text{ cm}^{-2}$. This confirms our mechanistic study, which shows that the UV photolysis of the palladium acetate film has occurred below the fluence threshold of the UV photodeposition and that this threshold is due to the desorption of the ligand and its photofragments leading to the deposition of palladium.

Acknowledgments

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