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# XPS and atomic force microscopy analyses of thin Au and Cu films on Pd

S. S. Maluf,<sup>1</sup> A. L. Gobbi,<sup>2</sup> P. I. Paulin-Filho<sup>1</sup> and P. A. P. Nascente<sup>1\*</sup>

<sup>1</sup> Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Via Washington Luiz km 235, 13565-905 São Carlos, SP, Brazil

<sup>2</sup> Laboratório Nacional de Luz Sincrotron, Rua Giuseppe Máximo Scolfaro 10000, 13083-100 Campinas, SP, Brazil

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The surface properties of bimetallic systems have been studied recently due to possible applications in different areas, such as electrochemistry, magnetism, and catalysis. Understanding of the atomic and electronic structures is crucial for designing metallic devices. In this work, thin films of gold and copper were grown on a polycrystalline palladium substrate by sputtering. For both films, the thickness was estimated to be 10 nm. The morphology of the films was investigated by atomic force microscopy (AFM). XPS was employed in order to verify the possibility of alloy formation. Oxide formation was observed for the Cu film, but not for the Au film. The copper oxide (CuO) was removed by argon ion sputtering. Alloying was not observed in the Au/Pd or Cu/Pd films. Copyright © 2004 John Wiley & Sons, Ltd.

**KEYWORDS:** thin film; gold; copper; palladium; XPS; AFM

## INTRODUCTION

In the past three decades a great deal of effort has been devoted to investigating bimetallic system surfaces, mainly since the development of surface-sensitive techniques.<sup>1–3</sup> The bimetallic systems which consist of transition and noble metals present interest in applications as catalysts.<sup>1,4</sup> In particular, bimetallic catalysts containing palladium and a noble metal are applied to several reactions,<sup>1,3</sup> and recent studies have demonstrated that the d bands of Cu, Ag, and Au are active in bimetallic bondings.<sup>5–12</sup>

The chemical and physical properties of thin metal films can be different from those of bulk metal surfaces.<sup>13</sup> Both Au–Pd and Cu–Pd systems form FCC continuous solid solutions, with the formation of ordered phases.<sup>14</sup> The growth of Cu films on single-crystal Pd surfaces was investigated by different techniques: on Pd(100), by scanning tunnelling microscopy (STM),<sup>15</sup> on Pd(110), by STM<sup>16</sup> and low-energy electron diffraction (LEED),<sup>17</sup> and on Pd(111), by XPS.<sup>18</sup> The behaviour of Au films grown on Pd(111) was studied by LEED and Auger electron spectroscopy (AES).<sup>19</sup>

In this paper we have investigated thin films of copper and gold on polycrystalline palladium substrate. The films were grown by DC sputtering, and characterized by atomic force microscopy (AFM) and XPS.

## EXPERIMENTAL SECTION

The polycrystalline substrates were made of palladium (99.99%) foils with thickness of 0.127 mm. The Cu and Au films were grown on Pd by DC sputtering, using a Balzers BA 510 instrument, with the following conditions: initial pressure of  $4 \times 10^{-5}$  Pa, partial pressure of argon of 0.4 Pa, sputtering current of 0.15 A, sputtering voltage of 0.9 kV, deposition rate of 0.05 nm/s, thickness of 10 nm, and deposition carried out at room temperature (approximately 300 K).

AFM analyses were carried out in contact mode, using a Digital Nanoscope IIIA instrument. The XPS measurements were performed in ultra-high vacuum (low  $10^{-7}$  Pa range) using a Kratos XSAM HS spectrometer. A non-monochromatic Mg  $K_{\alpha}$  ( $h\nu = 1253.6$  eV) was used as x-ray source, with power supplied by the emission of 10 mA at a voltage of 13 kV. The high-resolution spectra were obtained with an analyser energy of 20 eV. Argon ion flux was employed to sputter the surface. The Shirley background, mixed Gaussian/Lorentzian functions, and a least-square routine were used for the fitting to the peaks.

## RESULTS AND DISCUSSION

### XPS

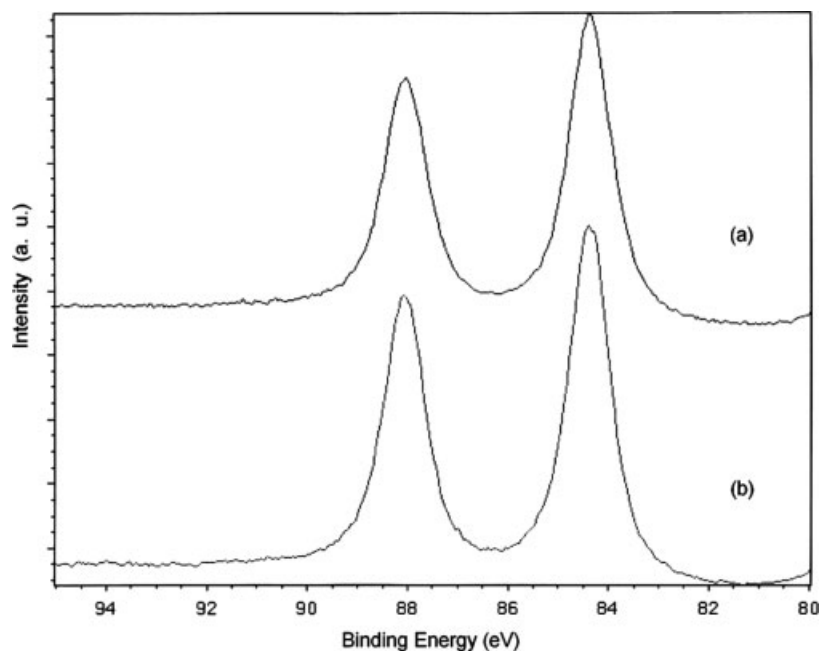
In Fig. 1, we display the Au 4f spectra of Au/Pd (a) before and (b) after the argon ion sputtering. Both spectra are very similar, with Au 4f<sub>7/2</sub> binding energy of 84.4 eV corresponding to metallic gold. Pd was not detected before the argon ion sputtering, suggesting that alloying did not occur. The interdiffusion in thin Au/Pd film was analysed by Bukaluk,<sup>20</sup> and the room temperature diffusion is estimated to be  $3.0 \times 10^{-18}$  cm<sup>2</sup>/s.

\*Correspondence to: P. A. P. Nascente, Universidade Federal de São Carlos, Departamento de Engenharia de Materiais, Via Washington Luiz km 235, 13565-905 São Carlos, SP, Brazil. E-mail: nascente@power.ufscar.br

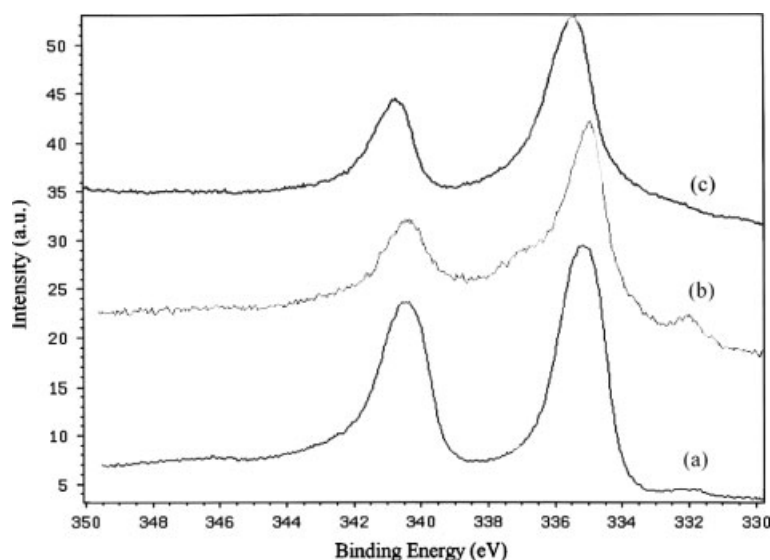
Contract/grant sponsor: Brazilian Synchrotron Light Source (LNLS); Contract/grant number: MIC 2127.

Contract/grant sponsor: FAPESP, Brazil; Contract/grant numbers: 00/13831-8; 01/14076-1; 02/03271-0.

Contract/grant sponsor: CNPq, Brazil; Contract/grant numbers: 477032/2001-0; 300968/91-4.



**Figure 1.** XPS Au 4f spectra of Au/Pd (a) before and (b) after argon ion sputtering.



**Figure 2.** XPS Pd 3d spectra, acquired after argon ion sputtering, of (a) palladium, (b) Cu/Pd, and (c) Au/Pd.

In Fig. 2, we present the Pd 3d spectra of (a) the palladium substrate, (b) Cu/Pd, and (c) Au/Pd. All three spectra were acquired after argon ion sputtering, indicating that both the Cu and Au films were partially eroded. The Pd 3d<sub>5/2</sub> peak at 335.1 eV, corresponding to metallic palladium, overlaps with the Au 4d<sub>5/2</sub> line (Fig. 2(c)) and with the Cu LMM line (Fig. 2(b)).

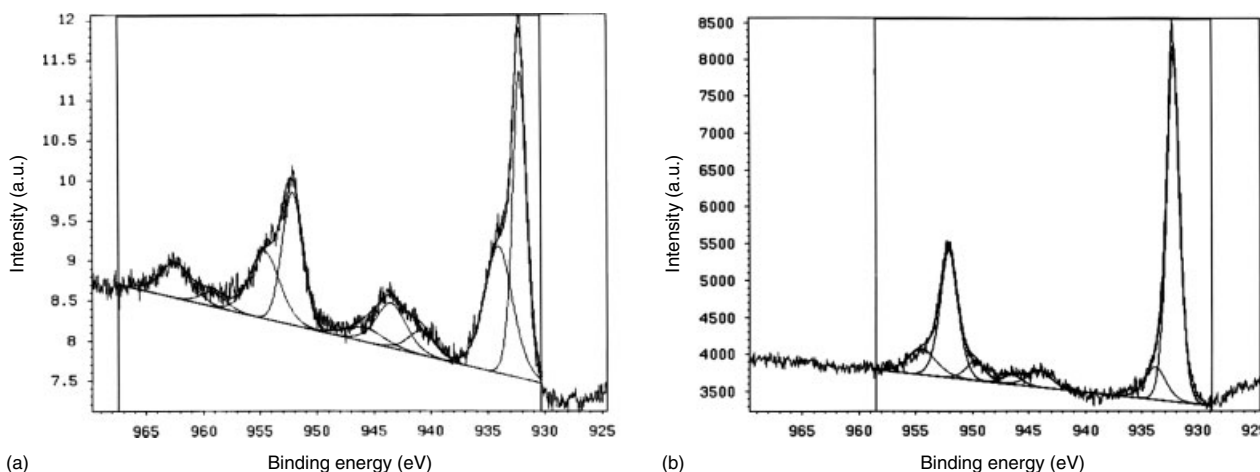
The Cu 2p lines are displayed in Fig. 3 for (a) non-sputtered and (b) argon sputtered Cu films deposited on Pd. For the argon sputtered film, the Cu 2p<sub>3/2</sub> peak is located at 932.3 eV, corresponding to metallic Cu. For the non-sputtered film, there are two components for the Cu 2p<sub>3/2</sub> peak, one at 932.3 eV (54 at.%) and the other at 934.3 eV (46 at.%). The satellite structure can be deconvoluted by components at 941.0 and 943.6 eV. The Cu 2p<sub>3/2</sub> component at higher binding energy and

the satellite structure can be attributed to Cu<sup>2+</sup> species (copper oxide and/or hydroxide).<sup>21</sup> The argon ion sputtering was effective in removing the oxide, as can be seen in Fig. 3(b).

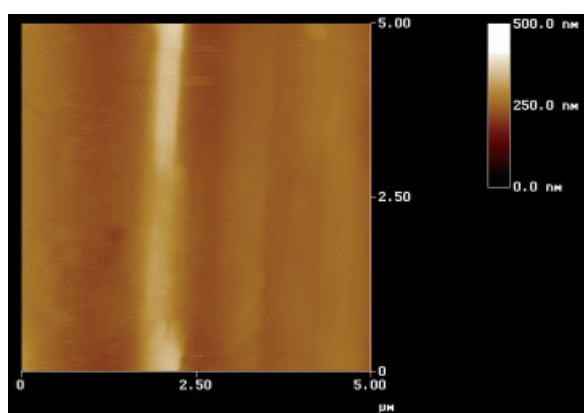
Likewise for the Au/Pd case, alloying did not occur for the Cu film deposited on Pd, since Pd was not detected before the argon ion sputtering. The interdiffusion in thin Cu/Pd film, at room temperature, was evaluated to be  $6.4 \times 10^{-25}$  cm<sup>2</sup>/s, according to Bukaluk's results.<sup>22</sup>

## AFM

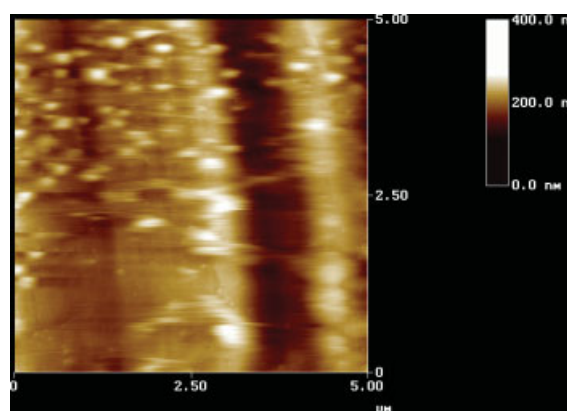
Figures 4 and 5 display the AFM images of the palladium substrate and the Au film deposited on Pd, respectively. It can be seen that the Pd surface is very flat (Fig. 4), and the lines are due to the rolling process. The deposition of gold on the Pd substrate did not cause changes in the



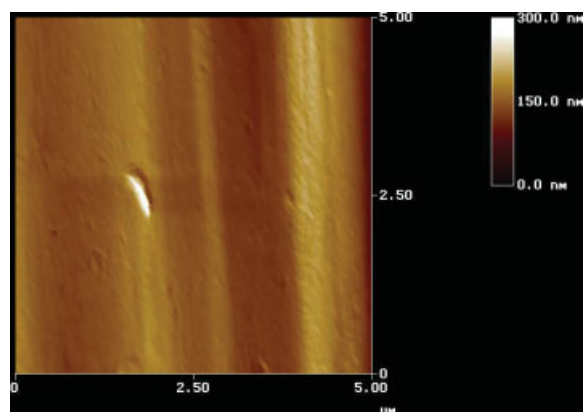
**Figure 3.** XPS Cu 2p spectra of Cu/Pd (a) before and (b) after argon ion sputtering. Fitting components are depicted.



**Figure 4.** AFM image of the Pd substrate (5  $\mu\text{m} \times 5 \mu\text{m}$ ).



**Figure 6.** AFM image of 100 Å Cu film on Pd (5  $\mu\text{m} \times 5 \mu\text{m}$ ).



**Figure 5.** AFM image of 100 Å Au film on Pd (5  $\mu\text{m} \times 5 \mu\text{m}$ ).

AFM image (Fig. 5), indicating that the Au film follows the Pd morphology. This statement is corroborated by the mean roughness amplitudes, which are similar for both Pd substrate (17.5 nm) and Au film on Pd (17.4 nm).

On the other hand, the morphology of the Cu film on Pd is different from the substrate one (Fig. 6). The surface is covered by small grains, which can be attributed to oxidized copper, since XPS revealed the CuO formation on the surface. The mean roughness amplitude is significantly higher (21.7 nm) than the one for the Pd substrate.

## CONCLUSION

The XPS results showed that an oxide and/or hydroxide was formed for the 10 nm Cu film on Pd, but not for the 10 nm Au film on Pd. The oxide was removed by argon sputtering, which also caused partial erosion of the films. The AFM images revealed that the Au film on Pd presented the same morphology as the palladium substrate, but the Cu film on Pd had a different texture, consisting of small CuO grains. For both systems, alloying in the film was not observed.

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## REFERENCES

1. Sinfelt JH. *Bimetallic Catalysts: Discoveries, Concepts and Applications*. Wiley; New York, 1983.
2. Bardi U. *Rep. Prog. Phys.* 1994; **57**: 939.
3. Rodriguez JA. *Surf. Sci. Reports* 1996; **24**: 223.
4. Campbell CT. *Ann. Rev. Phys. Chem.* 1990; **41**: 775.
5. Sham TK, Perlman ML, Watson RE. *Phys. Rev. B.* 1979; **19**: 539.
6. Watson RE, Davenport JW, Weinert M. *Phys. Rev. B.* 1987; **35**: 508.
7. Houston JE, Peden CHF, Feibelman PJ, Hamann DR. *Surf. Sci.* 1987; **192**: 457.

8. Sham TK, Yiu YM, Kuhn M, Tan KH. *Phys. Rev. B.* 1990; **41**: 1188.
9. Nascente PAP, De Castro SGC, Landers R, Kleiman GG. *Phys. Rev. B.* 1991; **43**: 4659.
10. Bzowski A, Sham TK. *J. Vac. Sci. Technol. A.* 1993; **11**: 2153.
11. Kuhn M, Sham TK. *Phys. Rev. B.* 1994; **49**: 1647.
12. Sammynaiken R, Kuhn M, Sham TK. *Physica B.* 1995; **208–209**: 371.
13. Koel BE, Sellidj A, Paffett MT. *Phys. Rev. B.* 1992; **46**: 7846.
14. Massalsky TB. *Binary Alloy Phase Diagram*. ASM International: Ohio, 1990.
15. Hahn E, Kampshoff E, Wälchi N, Kern K. *Phys. Rev. Lett.* 1995; **74**: 1803.
16. Barnes C, Gleeson M. *Surf. Sci.* 1994; **319**: 157.
17. Hahn E, Kampshoff E, Fricke A, Bucher J-P, Kern K. *Surf. Sci.* 1994; **319**: 277.
18. Liu G, Clair TPSt, Goodman DW. *J. Phys. Chem. B* 1999; **103**: 8578.
19. Baddeley CJ, Tikhov M, Hardacre C, Lornas JR, Lambert RM. *J. Phys. Chem.* 1996; **100**: 2189.
20. Bukaluk A. *Appl. Surf. Sci.* 1999; **144–145**: 395.
21. McIntyre NS, Sunder S, Shoesmith DW, Stanchell FW. *J. Vac. Sci. Technol.* 1981; **18**: 714.
22. Bukaluk A. *Vacuum* 1999; **54**: 279.