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Auger Studies of Electroless Nickel Films

R. C. BAETZOLD AND R. E. MACK

Research Laboratories, Eastman Kodak Company,
Rochester, New York 14650

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Auger electron spectroscopy (AES) shows that Pd nuclei obtained by evaporation onto glass are contaminated by S, C and possibly O during air exposure. AES also shows that nickel deposited electrolessly covers such nuclei and that nickel continues to be deposited even when the Pd is completely covered. Apparently both contaminated palladium nuclei and nickel-covered palladium play a catalytic role in electroless deposition of nickel.

I. INTRODUCTION

Auger spectroscopy provides a means of learning the elemental composition of surfaces and is therefore of interest in catalytic studies. The technique is particularly useful for studying the mechanism of catalysis in metal systems, which we plan to illustrate for the case of electroless deposition. Recently, Hamilton and Logel (*1*) have investigated the role of small palladium nuclei in the electroless deposition of nickel (*2,3*). They find that a palladium nucleus prepared by vacuum deposition and consisting of more than four to six atoms is required to initiate the deposition of nickel from a solution of the reducing agent dimethylamineborane (*2*) and nickel ion. This identification of a critical size of palladium nucleus required for catalysis was accomplished by an electron microscopic study of the nucleation and growth of the metal deposits.

The variation of catalytic activity of small metal nuclei with size is a topic that has been of interest for a long time (*4–6*). Depending upon the reaction type, the catalytic activity may be an increasing or decreasing function of size. A program to understand the electronic structure of metal nuclei by molecular orbital calculation (*7,8*) has been underway and provides information on the variation of properties with size. The presence of vacant *d* molecular orbitals could account for the beginning of catalytic activity at a size of four to six atoms. However, the role of the palladium nuclei in the reaction must be understood in order to better determine which factors might be influenced by the electronic properties of the palladium nuclei.

The role of the palladium nuclei in electroless nickel deposition is examined in this report. One question concerns the valence state of the palladium nuclei and what impurities may be on their surface. The second question concerns the role of the palladium during the time when nickel is deposited. Does the palladium become covered with nickel? If so, the electroless nickel film may be autocatalytic. Is it possible that the palladium diffuses through the depositing nickel to the aqueous interface to catalyze the continuing deposition? This question is easily answered since the measured coverage of Pd atoms of 5×10^{14} atoms/cm^2 required for continuous nickel-film deposition (*1*) is well within the detection capabilities of the Auger instrument.

Recently the Auger technique has been used to determine the bonding characteristics of electrodeposited nickel (*9*). Metal impurities, including Ag and Cu, which codeposit with the nickel film, were identified in the films and correlated with the embrittlement of these films. This technique demonstrated the presence of the Ag impurity in a thin layer along the fracture region.

II. TECHNIQUE

The Auger technique has been described recently in several reviews (*10,11*). An electron beam of 1–5 kV is directed towards a sample and the first derivative of the kinetic-energy distribution of the excited Auger electrons is measured. The kinetic energies are analyzed in the cylindrical mirror analyzer, which permits sweeping of an entire spectrum in milliseconds. Our commercially available equipment (Physical Electronics Industries) analyzes a spot of 50-μm diameter and 2–5 atomic layers deep. Samples are analyzed in a bell jar with pressure in the ultrahigh vacuum range so that surface cleanliness once achieved can be maintained. A sputter ion gun producing a beam of Ar^+ or Xe^+ ions is used to etch away the sample at a rate of 10–15 Å/min and can be used simultaneously with Auger analysis to obtain a depth profile of the elements in a sample.

While several problems exist in the quantitative determination of surface concentration of Auger spectroscopy, it is desirable to have a rough measure of surface composition. We have employed the formula (*12*):

$$C_x = \frac{P_x/Q_x}{\Sigma_i P_i/Q_i}, \qquad (1)$$

where C_x is the fractional surface concentration of element x, P_x is the peak-to-peak height of element x in the observed spectrum, Q_x is peak-to-peak height of element x in pure material, and the summation extends over each element observed in the spectrum.

All films and nuclei were prepared by techniques described in other work (*1,2*). After drying, the films were exposed to atmosphere for various lengths of time before introduction into the Auger equipment. The electroless plating solutions consisted of a reducing agent (dimethylamineborane, 1–3%), a nickel salt ($NiCl_2$, 0.1 *M*), and a complexing agent (gluconic acid, 0.6 *M*) at pH 9.0.

III. RESULTS

A. Palladium Nuclei

The Auger spectrum of evaporated palladium nuclei, which are catalytic for

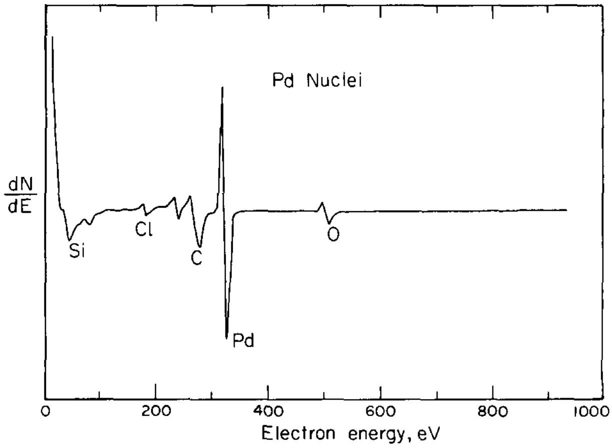

FIG. 1. Spectrum of Pd nuclei on glass slide.

nickel deposition, is shown in Fig. 1. The equivalent of approximately 10 monolayers was evaporated on the glass slide support. We should like to point out that this catalytic surface contains several elements including O, Pd, C, Cl, and Si. The O and Si are present in the glass substrate. An analysis of the surface according to Eq. (1) gives the following composition: C = 33%; Pd = 56%; O = 5%; Cl = 3%, Si = 3%. The source of C contamination is most likely atmospheric, and Si and O signals are due to regions of the glass not covered by Pd. B is contained in the reducing agent used, but its presence may be masked by the Cl since Auger signals from B and Cl occur at very close energies (B = 179 eV, Cl = 181 eV). In samples such as this where both elements are likely to occur, the analysis must be made by curve shape. An amount of contamination covers the Pd nuclei, as can be shown by the observation that the Pd signal increases when material is sputter-etched from the surface. A sputter-etch of 15 sec at 5×10^{-5} Torr Xe removes approximately a 4-Å thickness of atoms. This procedure produces an increase in the Pd, Si, and O signal and decreases the C and Cl signal.

The Auger spectrum has been recorded versus amount of Pd evaporated on the glass slides. Figure 2 shows that the Pd Auger signal is proportional to coverage up to half the pure Pd signal. In addition, the C signal decreases as the Pd signal decreases, which suggests that C may be associated with the Pd. The Si signal due to the glass substrate increases as the Pd coverage decreases.

An estimate of the sensitivity of the Auger technique for Pd can be made from Fig. 2. At an equivalent coverage of 5.7×10^{14} Pd atoms/cm², the signal-to-noise ratio is 50. Since this coverage is about 0.5 monolayer, 1% of a monolayer of Pd is the detection limit under these conditions. The Pd may be covered by C so this detection limit is only an upper estimate.

B. Nickel Films

Nickel films deposited by electroless deposition were analyzed by Auger spectroscopy to determine the catalytic role of Pd nuclei. We have observed films in which the amounts of Ni deposited are varied up to an average Ni thickness of 100 Å. (Fig. 3) Such a Ni film is still discontinuous and we can observe signals due to Pd, Si, and O (Pd nuclei evaporated on a glass substrate), indicating that some Pd

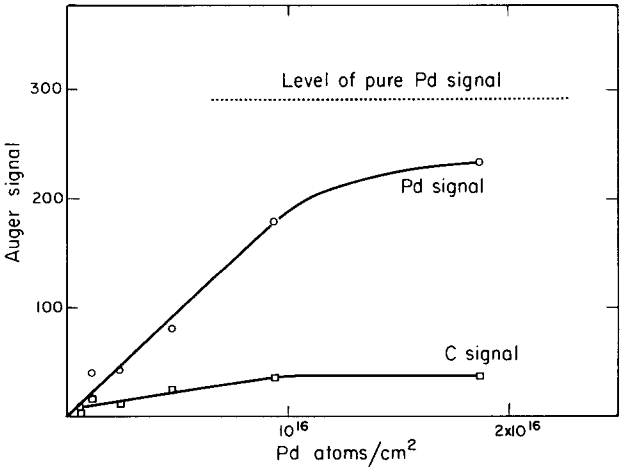

FIG. 2. Plot of Pd and C Auger signal versus amount of Pd evaporated.

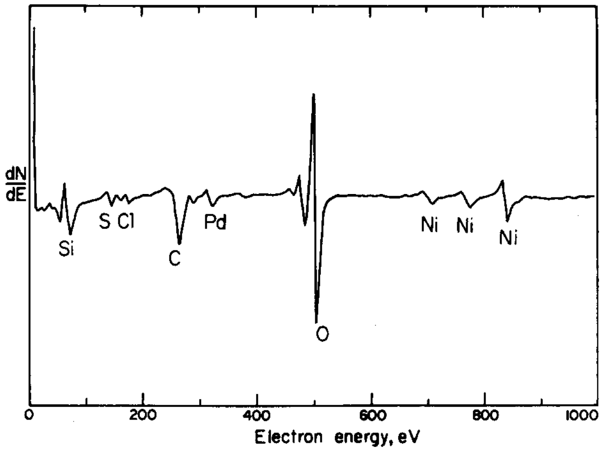

FIG. 3. Spectrum of Ni film partially covering Pd nuclei.

nuclei are not covered by Ni. After several hundred angstroms of Ni are deposited, no Pd signal is present on the surface, as shown for such a film in Fig. 4. Apparently the Pd is covered by the Ni and the reaction can proceed even when the original catalytic surface is covered. Several impurities are located on the film surface, including O, C, Cl, and S. The signal due to each of these impurities decreases as the film is sputtered; however, significant amounts of these impurities could be introduced during electroless deposition.

We have recorded the Auger spectrum of the Ni films during sputter-etch treatment. With this procedure, the elemental analysis as a function of depth into the film is recorded as in Fig. 5. Note that C, O, Cl, and S impurities are distributed throughout the film. It is clear that such a film would behave differently from a pure Ni film, and the regulation of impurities could have a large effect on film properties. Signals due to Pd appear at a depth of 2700 Å. We do not know the relative sputtering rates of the various elements in this profile, but we have not seen evidence for Pd being inefficiently sputtered relative to nickel as a means of accounting for its appearance in Fig. 5. Continued sputtering

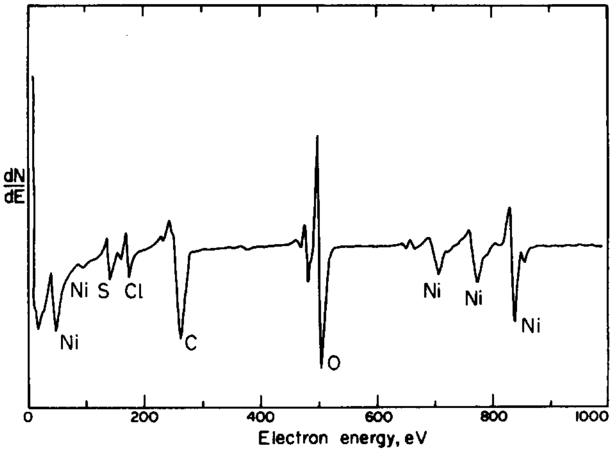

FIG. 4. Spectrum of Ni film 2000 Å thick physically deposited.

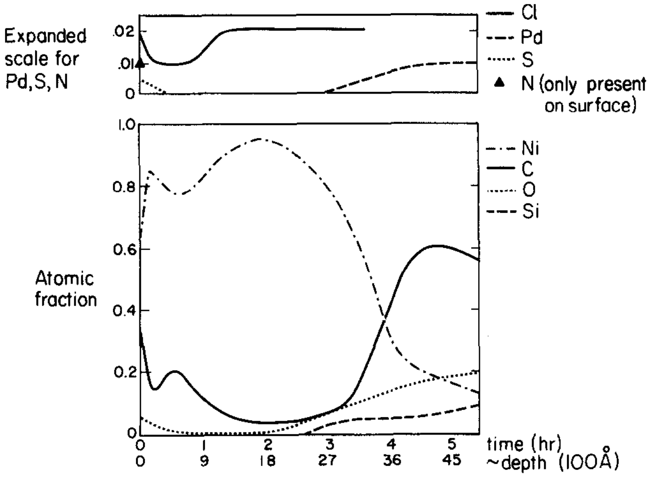

FIG. 5. Depth profile of a nickel film plated on glass after successive vacuum depositions of carbon and palladium.

shows a decrease in Pd signal. Note that in-depth resolution of the Ni–glass interface is not as sharp as one would expect. This is because: (a) the glass surface has a certain amount of roughness to it and (b) the sputtering process causes some surface homogenization that causes the apparent composition profile to be more diffuse than the real profile.

C. *Palladium Films*

Continuous evaporated palladium films have been studied since their surface contaminants might be expected to be similar to the surface contaminants on palladium nuclei. Palladium films are easily contaminated by carbon and sulfur, but do not react readily with oxygen. Figure 6 is the spectrum of a Pd film that has been exposed to the atmosphere and O, C, and S have been adsorbed to the surface. Sputtering the film removes this surface layer and the associated impurities, as shown in the spectrum in Fig. 7. When such a Pd film with a clean surface is heated in the vacuum chamber (10^{-9} Torr) using an electron beam, S reappears on the surface. Bulk S, present in low concentration, be-

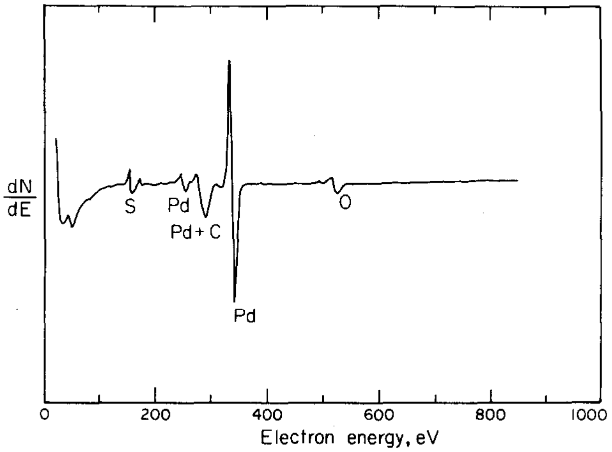

FIG. 6. Spectrum of Pd film exposed to atmosphere.

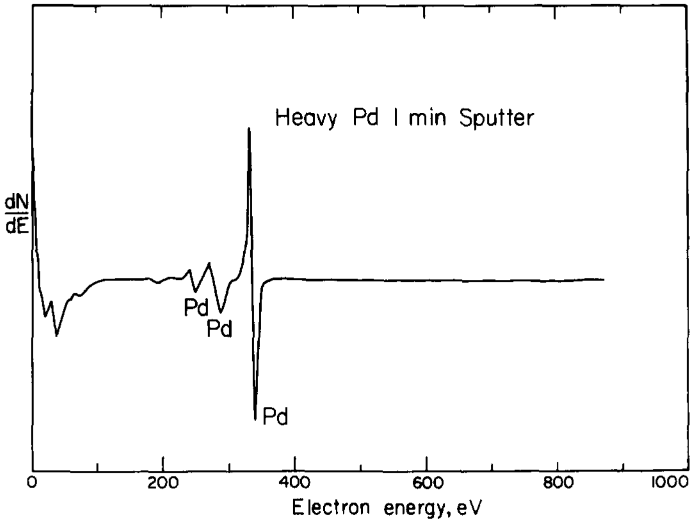

FIG. 7. Spectrum of Pd film sputtered 1 min.

comes mobile at high temperature and accumulates on the Pd surface. A gentle sputtering of this surface removes all S, indicating that it is present in a layer less than 10 Å thick.

Oxygen does not react readily with clean palladium films at room temperature or higher temperatures. Pure oxygen is admitted to a pressure of 5×10^{-5} Torr in the vacuum system and the film is heated to near melting. The Auger spectrum of the Pd surface shows no oxygen after exposure for several hours or after heating the Pd in the presence of O_2. Oxygen has only been observed on Pd surfaces when carbon is also present. Thus, O may be adsorbed on a carbon layer, itself adsorbed to the Pd, or an oxide of C may be the adsorbed species. Most likely the electron beam would decompose such an adsorbed C-oxide molecule.

IV. DISCUSSION

The Auger technique has shown that during deposition the nickel films cover the palladium catalyst. The freshly formed electroless nickel thus becomes the catalytic surface for further deposition. The composition profiles in Fig. 5 show that the nickel deposited is not pure and that a substantial amount of carbon is present.

The surface of palladium films becomes contaminated easily by exposure to atmosphere. Elements such as S, C, and O were detected. It is interesting that S, known to be a poison for some reactions, can be present in small amounts on the nuclei and not prevent the deposition. Our studies do not support the possibility that the small palladium nuclei may be present as an oxide.

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