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Behavior of Pd/Sn and Pd Catalysts for Electroless Plating on Different Substrates Investigated by Means of Rutherford Backscattering Spectroscopy

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ratio of 12/1 be employed for silox CVD processing. (*iii*) The deposition rate decrease with increased flow of nitrogen is attributed to two factors, depression of the silane partial pressure and lowering of the wafer surface temperature.

Acknowledgments

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Behavior of Pd/Sn and Pd Catalysts for Electroless Plating on Different Substrates Investigated by Means of Rutherford Backscattering Spectroscopy

Leo G. Svendsen

Institute of Physics, University of Aarhus, DK-8000, Aarhus C, Denmark

Tetsuya Osaka*

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo, Japan

Hideo Sawai

OKI Electric Industry Company, Limited, Materials Department, Research Laboratories, Hachioji-shi, Tokyo, Japan

ABSTRACT

Two catalytic systems for electroless metal deposition have been investigated by means of Rutherford backscattering spectrometry (RBS). The well-known tin sensitizer, palladium activator, two-step catalyst had the main emphasis, but also a commercial one based on evaporated palladium was examined. The behavior of the two-step catalyst was largely dependent on the substrates used. On Al_2O_3, the Sn:Pd ratio was 1:1 with 1.3×10^{15} atoms/cm² each. On carbon substrates, the Sn:Pd ratio was 1:4 with 6×10^{15} tin atoms/cm² and 24×10^{15} palladium atoms/cm². Both these results violate the simple reaction mechanism described by the equation $Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0$. The commercial catalyst on polyimide containing 2.5×10^{15} palladium atoms/cm² on the surface behaved differently compared to the two-step catalyst by diffusing into the deposited layer and thereby influencing its deposition rate.

The catalyst systems used for initiating the deposits from autocatalytic Ni-P and Ni-P-W baths have been investigated by means of Rutherford backscattering spectrometry (RBS). The results thus obtained may contribute to the current discussion of this subject. This article reports on two types of catalysts, *i.e.*, the well-known two-step sensitizer-activator system containing Sn^{2+} and Pd^{2+} and a commercial method, where catalyzing takes place by means of a sparse layer of evaporated palladium atoms.

Previously, the two-step system has been investigated by Meek (1, 2) using RBS as well as the mixed catalyst system (3). Meek found results in agreement with those obtained by Cohen *et al.* (4), using Mössbauer spectroscopy; they stated that the simple reaction

$$Sn^{2+} + Pd^{2+} \rightarrow Sn^{4+} + Pd^0 \qquad [1]$$
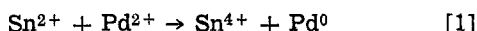
takes place to make the surface catalytically active. These findings were actually in disagreement with those of de Minjer *et al.* (5) as well as with those from the photosensitive sensitizers based on both Sn^{2+} and Sn^{4+}, neither of which could be explained by the

* Electrochemical Society Active Member.
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simple Eq. [1] only. The latter results are mainly obtained by Schlesinger *et al.* (6-9).

The RBS Method

When a surface is bombarded with swift $^4He^+$ ions, the scattered particles can yield information on the stoichiometry *vs.* depth in the surface layer. The spectra consist of the number of particles as a function of the particle energy after scattering, shown in Fig. 1. From the width of a peak, the layer thickness may be determined, while the peaks stemming from the same layer contain information on the stoichiometry. As seen in Fig. 1, this is phosphorus and nickel in the top layer and aluminum and oxygen in the substrate. After a deposition time of 40 sec, the dotted spectrum in Fig. 1 indicates that a layer of a certain thickness has been formed on the substrate. The retrograde movement of the signals stemming from oxygen, aluminum, and Pd/Sn is due to their staying in-depth, whereas the nickel and phosphorus peaks always start at the same position, indicating signals from the surface. The tail is due to an in-depth deposition on the substrate.

In Fig. 1, the insert shows the experimental setup. An area of 1×1 mm² of the surface is irradiated by 2 MeV $^4He^+$ ions to a dose of 40 μC. The investigation
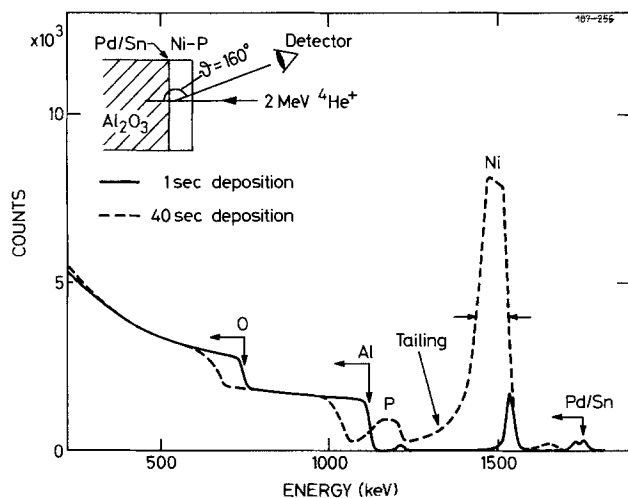
Fig. 1. RBS spectra of Ni-P(b) layers on top of sintered alumina substrates. The backward movement of some signals is indicated by "←↓."

was made under a pressure below 5×10^{-7} Torr. The scattered ions are detected by a surface-barrier detector at an angle θ of 160°. A detailed description of the equipment and software used in this investigation is given in Ref. (10), and for an introduction to the RBS method, the reader is referred to Ref. (11).

Experimental

Three types of substrates were used in the investigation, i.e., (i) alumina, a sintered 96 weight percent (w/o) α-Al_2O_3 ceramics[1] often used for hybrid IC substrate; (ii) carbon, as 99 w/o pure graphite containing a phenol-resin binder;[2] (iii) a type of polyimide[3] used for flex-print substrate. The alumina and carbon substrates were degreased with ethanol, rinsed in water, and dried prior to being made catalytic for nickel deposition. This was done in the following way: sensitization: 2 min, rinse 10 sec; activation: 2 min, rinse 10 sec; sensitization: 2 min, rinse 10 sec; activation: 2 min, rinse 10 sec. Deionized water was used for rinsing, and the solutions were made as follows: sensitizer: $SnCl_2 \cdot 2H_2O$, 1 g/liter; HCl 37%, 1 ml/liter; activator: $PdCl_2$, 0.1 g/liter; HCl 37%, 0.1 ml/liter. The repeated two-step process[4] was used because of its superior catalytic effect on alumina substrate compared to those of a mixed $PdCl_2/SnCl_2$ catalyst. To compare the results, the same procedure was applied to graphite to make the substrate catalytic. The catalyst thus made is denoted "A catalyst." The polyimide was catalytic when purchased. This has been done by evaporating palladium sites onto one side of the specimens, and this catalyst is denoted "B catalyst."

When the substrates had been made catalytic, nickel was deposited from one of the following baths: Ni-P (a): a commercial bath[5] with pH = 5.2 and hypophosphite as a reductant; Ni-P(b): pH = 9.0 and with the following composition: 0.027 M/liter $NiSO_4$, 0.068 M/liter Na_3-citrate, 0.227 M/liter $(NH_4)_2SO_4$, 0.066 M/liter NaH_2PO_2; Ni-P-W: same composition and pH as Ni-P(b) plus 0.106 M/liter Na_2WO_4.

All the baths were operated at 90°C, and the samples were dipped into the hot baths for different periods of time to find the deposition rate. The electroless Ni-

[1] From Nippon Tokushu Togyo Company, Limited (NGK Spark Plug Company Limited).
[2] From Nippon Carbon Company, Limited.
[3] From Tore Company, Limited, film thickness of polyimide used is 75 μm.
[4] Since alumina substrate is a difficult-to-plate substrate, the catalization carried out only by a mixed catalyst is not sufficient to form the basis for a uniform electroless nickel film. This repeated two-step process is effective for alumina. It is sometimes used for alumina substrate in practical use, e.g., at the Precision Electronic Components Limited, Toronto, Ont., Canada
[5] NICKA 311 from Kaseihin-Kogyo Company, Limited.

P-W film has previously shown (12) some superior properties concerning the uniformity and the thermal stability of film resistance compared to a film precipitated from the Ni-P(b) bath, although the baths are differing only in that the Ni-P-W bath contains Na_2WO_4.

Results

Below, descriptions are given of the results that were achieved concerning the catalysts.

Composition and content.—In Fig. 1, only palladium and tin give visible signals stemming from the A-type catalysts. Any signal from the oxygen that may be present due to a tin-oxo compound can be detected neither on alumina nor on graphite substrates because of interfering signals (on graphite, these are caused by the oxygen content in the phenol resin binder). Chlorine, on the other hand, should be easily detectable at a position 80 keV above the phosphorus peak in Fig. 1, but no peak is present in any of the spectra. This is a general result, and the investigations show that the amount of chlorine adhering to the surface must be less than 12% of the original chlorine content in $SnCl_2 \cdot 2H_2O$ and $PdCl_2$. It may therefore be concluded that after 1 sec of deposition, the amount of chloride ions following the adhering tin and palladium is insignificant.

RBS gives the following ratios and contents for Pd/Sn:

Alumina substrates: Pd/Sn ratio 1:1 within 15%. Content for both palladium and tin: $1.3 \pm 0.3 \times 10^{15}$ atoms/cm².

Carbon substrates: Pd/Sn ratio 4:1 within 20%. Palladium content: $24 \pm 2 \times 10^{15}$ atoms/cm². Tin content: $6 \pm 1 \times 10^{15}$ atoms/cm².

Polyimide: palladium content: $2.5 \pm 0.3 \times 10^{15}$ atoms/cm².

The findings were unaffected by the baths used for covering the surface with a thin, conductive Ni-P layer. Figure 2, I and II show that 1 sec in the acidic Ni-P(a) bath and 1 sec in the basic Ni-P-W bath result in the same peaks in the RBS spectra. The substrates, on the other hand, greatly affect the Pd/Sn ratio and content. A comparison between the RBS peak of Pd/Sn on alumina and on carbon given in Fig. 2 demonstrates the difference of the catalyst.

Behavior of the catalysts.—Figure 3 shows a figure series of the behavior of the two-step A catalyst on alumina and on the evaporated palladium catalyst the B catalyst. It is found that the two types of catalysts behave differently with respect to a deposited Ni-P layer from the Ni-P(b) bath. The spectra of the two-step process indicate that the catalyst gradually becomes situated in greater depth as the deposition proceeds, whereas the spectra of the evaporated catalyst show that it moves both in the precipitated layer and is present at the very surface.

The results in Fig. 4 show that catalyst A remains at the interface since the deposition rate is the same when measured at the nickel peak and at the Pd/Sn peak. This result holds for catalyst A for all baths and both substrates under investigation. The error bars in Fig. 4 include the uncertainty referring to the measuring system only (the RBS equipment), i.e., the uncertainty stemming from the experimental procedure is not registered.

Influences of the catalysts.—Figure 3 shows that palladium remains at the very surface when catalyst B is used. This may be the reason for the considerable change in deposition rate in the earlier stages. On polyimide, the Ni-P(b) bath deposits at a rate of 40% only of that on alumina when the other conditions are identical, and the Ni-P-W bath has reduced its deposition rate to only 30% of that on alumina. However, until catalysts A and B have been investigated on the same type of substrate, other explanations cannot be fully excluded.
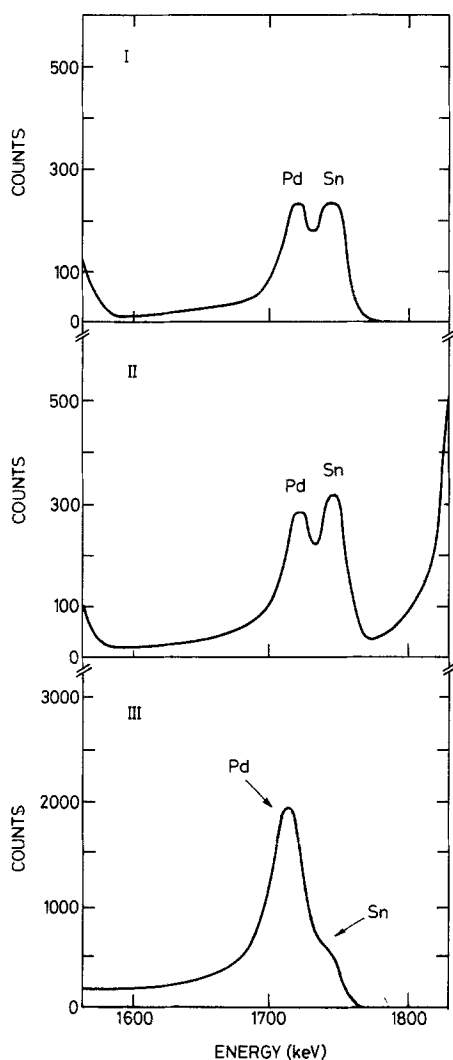
Fig. 2. RBS signals from catalyst A on Al_2O_3 (I and II) and from catalyst A on C (III). I, 1 sec deposit in Ni-P(a) bath; II, 1 sec deposit in Ni-P-W bath; III, 3 sec deposit in Ni-P(b) bath.

Discussion and Conclusion

The use of RBS for obtaining information on the two-step Pd/Sn catalyst and the commercial palladium catalyst has successfully added to what we already know.

The fact that chlorine is missing on the substrate surface means that tin is present in an oxygen compound. This is in agreement with Ref. (5 and 13) and
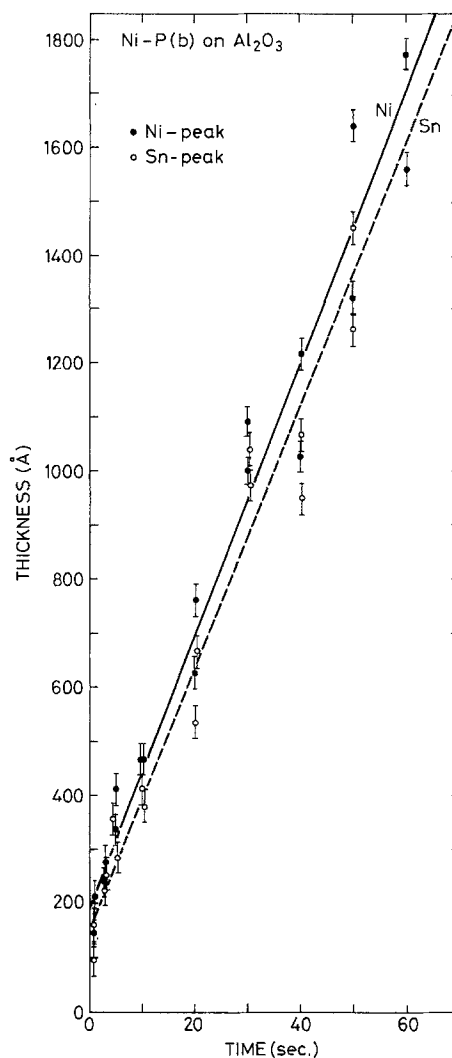

Fig 4. Relation between deposition time and the thickness of Ni-P(b) layer on Al_2O_3. The thickness is found by the width of the Ni peak and the backward movement of the Sn peak in the RBS spectra. Two linear relations are as follows: thickness (in angstroms) $= 24.7 \pm 1.1 \times$ sec $+ 207 \pm 36$, and $23.6 \pm 1.3 \times$ sec $+ 162 \pm 34$.

is also in agreement with Ref. (1) when the discussion in Ref. (6) is borne in mind. Here it is stated that very diluted sensitizer solutions consist mainly of oxo-compounds, whereas the more concentrated ones also contain chlorine. The sensitizer used in the present investigation must be rather dilute compared to that
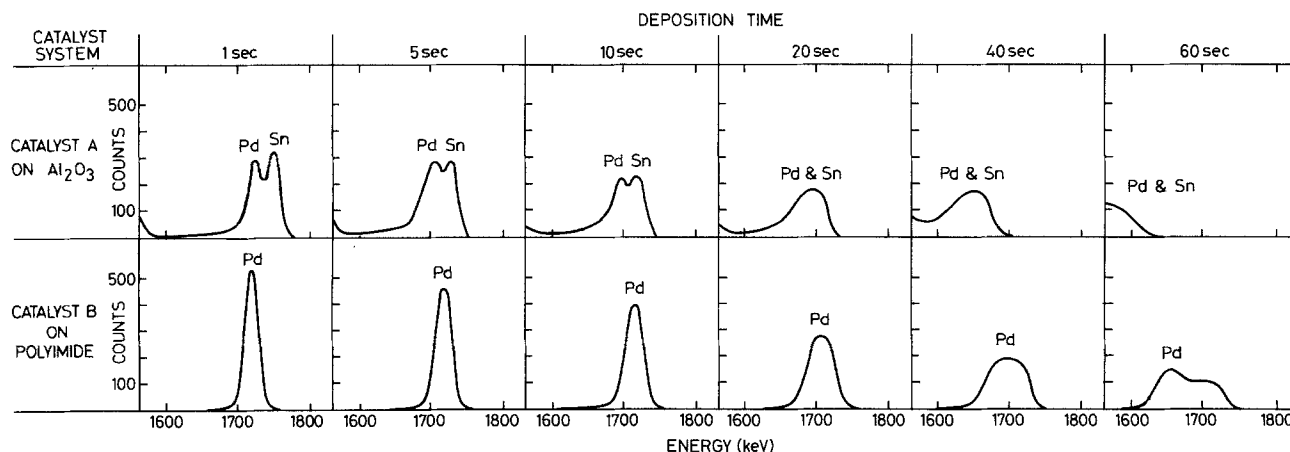

Fig. 3. RBS signals from catalysts A and B when the Ni-P(b) is deposited on the surface. As deposition proceeds, the signals from catalyst A move toward lower energies. The signals from catalyst B broaden and always start at the same position in the different spectra.

used in Ref. (1), which contains 16 g/liter SnCl$_2$ · 2H$_2$O and that in Ref. (6) containing 7 g/liter. In Ref. (5), the very dilute sensitizer containing only 0.1 g/liter was used. A tin concentration on graphite of 6 × 10^{15} atoms/cm^2 is smaller than the 11 × 10^{15} atoms/cm^2 on graphite found in Ref. (1), however, the difference is not so large, considering the differences of the sensitizers and the activating process. The palladium concentration of 1.3 × 10^{15} atoms/cm^2 found on the alumina is somewhat larger than that of 0.9 × 10^{15} atoms/cm^2 on glass substrate in Ref. (1). Reference (1) agrees with the catalyst remaining on the interface. However, the amount of palladium on carbon is almost ten times greater than that found in Ref. (1), and the ratios Pd:Sn of 1:1 and 4:1 on alumina and graphite both violate Eq. [1] when it is borne in mind that most of the tin must be in the form of Sn^{4+} according to Ref. (4 and 13). The result means that it is not a simple redox process. This result is not unique for alumina and carbon. Reference (14) reports similar results for polymer surfaces. The substrate species is concluded to control not only the concentration of adsorbed catalyst but also the ratio of Pd:Sn.

Two other discrepancies were found for system A. Neither a large dissolution of tin ions into the metal bath nor the migration of the catalyst into the deposits was found, as in Ref. (1). Whereas, the results on the B catalyst on polyimide showed that the migration of palladium into the deposited layer takes place.

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Chemically Deposited Ni-P and Ni-P-W Layers Investigated by Means of Rutherford Backscattering Spectrometry

Leo G. Svendsen

Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark

Tetsuya Osaka* and Ichiro Koiwa

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo, Japan

Hideo Sawai

OKI Electric Industry Company, Limited, Materials Department, Research Laboratories, Hachioji-shi, Tokyo, Japan

ABSTRACT

Information on the deposition of Ni-P and Ni-P-W from autocatalytic baths has been obtained by means of Rutherford backscattering spectrometry (RBS). Measurements of the kinetics during the first 60 sec of precipitation established the deposition rate to be highly dependent on the catalyst used. The Ni-P-W bath precipitates at a lower rate than do the various Ni-P baths. The investigation on the stoichiometry indicates that the codeposition of phosphorus on an average decreases from 10.0 to 3.1% when tungsten is present in the layer. For brief deposition periods (1 and 3 sec), the phosphorus content is found to be higher than the average. The phosphorus content in the first 500Å of a layer seems to be increased compared to the layer average; however, this result is on the detection limit of the RBS method.

Electroless nickel is by far one of the most utilized of all electroless-bath systems. Previously, the deposit from autocatalytic nickel baths has been investigated in a variety of ways, ranging from pure chemical methods (1) to x-ray (2) and electron beam based spectroscopy (3, 4). Rutherford backscattering spectrometry (RBS) has been applied to the examination of the kinetics of copper deposits (5, 6) and the composition of the catalysts used for electroless deposition (7-9), but so far, there have been few reports on RBS analysis of electroless nickel layers (10).

The present paper discusses the results obtained by RBS as far as both the kinetics and the stoichiometry of various deposited Ni-P and Ni-P-W layers are concerned.

Analytical Method

Reference (9) gives a very brief introduction into the field of RBS. With this method, knowledge of the surface is obtained by irradiating a specimen with swift monoenergetic light ions and measuring the yield of the ions backscattered an angle θ. The method is nondestructive and yields information on stoichiometry vs. depth (from the surface of the specimen) down