

Fig. 7. SIMS profiles for CoP on NiP: a) NiP pretreatment in a NaOH solution in D<sub>2</sub>O; b) electroless NiP plated from D<sub>2</sub>O.

At least some of the oxygen appears to be incorporated in the form of a hydroxide. There is also mobile hydrogen in the structures. The  $H_2$  gas evolved from the decomposition of  $H_2PO_2^{-}$  during electroless deposition is probably incorporated in the deposit as this mobile hydrogen.

A rinse between the NaOH pretreatment and the CoP deposition does not reduce the amount of interfacial oxygen and does not improve the macromagnetic properties of the CoP layer. The source of the interfacial O is thus concluded to be an oxidation of the NiP during the pretreatment. It was shown that the early stages of the CoP deposition cannot account for the observed incorporated 0.

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# Oxygen-Diffusion-Size Effect in Electroless Metal Deposition

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## ABSTRACT

Experimentally there appears to be a limit to the size of isolated patterns of electrocatalytic nuclei below which electroless metal deposition does not occur. From a model of electroless deposition on small isolated circular spots we conclude that this inhibition effect is caused by an enhanced supply of oxygen to small patterns due to nonlinear diffusion of dissolved oxygen. Since generally the kinetically determined rate of oxygen reduction is larger than that of oxidation of the reducing agent, the open-circuit potential of nuclei in small patterns cannot be shifted to a sufficiently negative value at which metal deposition is initiated. At relatively large substrates with a high density of small patterns this so-called oxygen-diffusion-size effect may not be noticed since the supply of oxygen is limited by linear diffusion to an effectively planar substrate.

In the past decade selective electroless metal deposition has attracted considerable attention for application in the fabrication of microelectronic devices, printed circuit boards and imaging systems [see for example Ref. (1-6)]. Electroless metal deposition can be carried out selectively since deposition is autocatalytic and requires an electrocatalytic surface to start. Since in most cases the substrate surface is not sufficiently electrocatalytic to initiate electroless metal deposition, it is necessary to activate the surface. Usually, this is accomplished by the selective application of electrocatalytic metal nuclei on the substrate, for example, by photoselective activation procedures (1-2).

Recently, we started to investigate the initial stages of electroless metal deposition on semiconductor substrates on which electrocatalytic metal nuclei were previously locally photodeposited by use of a focused laser beam (7-9, 12). It was observed that there is a critical size of isolated spots below which autocatalytic metal deposition either does not occur or becomes inhibited after a short time.

This paper aims to elucidate this size effect which implies a limit to the size of electrocatalytic patterns below which electroless metal deposition may not occur. After the experimental section, some experimental observations are first reported to clarify this size effect. Then a simple model of electroless deposition on isolated spots is considered. Subsequently some experimental justification of two basic assumptions in the model is given. Finally, the size effect is discussed using mixed potential theory.

#### **Experimental**

Solutions.—Table I gives the compositions of the aqueous solutions (A-K) which were used for (i) electroless deposition of Ni (A, B), Cu (C, D), and Au (E); (ii) Pd photodeposition on TiO<sub>2</sub> films (F); (iii) Sn-Pd activation of glass substrates (G, H, I); and (iv) electrochemical measurements (J, K). Sn-Pd nuclei were deposited on a substrate surface by dipping a clean substrate successively in solutions G, H, and I (10). Each dip lasted 1 min and was followed by a dip in water for 1 min. All solutions were prepared from triply distilled water. Unless otherwise stated, experiments were carried out at room temperature and no gas was bubbled through the solution.

Materials.-Thin polycrystalline TiO2 (anatase) films with a thickness of  $\approx 50$  nm were deposited on a glass plate  $(50 \times 50 \times 1 \text{ mm}^3)$  by spin-coating and pyrolysis of titanium acetylacetonate. Thin (<10 nm) TiO<sub>2</sub> films on thin (13 nm) supported amorphous Si<sub>3</sub>N<sub>4</sub> membranes were used for transmission electron microscopy (TEM) measurements and were also produced by this method (11). TEM measurements were also performed on thin (≈30 nm) supported amorphous SiO<sub>2</sub> membranes which were produced by similar photolithographic techniques as described previously for Si<sub>3</sub>N<sub>4</sub> membranes (11). Glass substrates were tapering glass rods and glass fibers with diameters ranging from 30 to 1000 µm. p-GaAs electrodes were constructed from zinc-doped (100) GaAs single-crystal wafers with a carrier density of  $\approx 10^{17}$ /cm<sup>3</sup> which were obtained from MCP Electronics (9). Various Pd microcylinder electrodes with a length of 1 cm and diameters ranging from 10 to 500 µm were made from Pd wires with a purity of 99.9% obtained from Goodfellow.

Equipment.—Local UV illumination of substrates in a quartz cell was carried out by focusing a laser beam or projecting a homogeneously illuminated circular aperture on the substrate surface (7, 9, 12). In either case a continuous argon ion laser (Spectra Physics Model 2025-05; wavelength 351.1-363.8 nm) was used. TEM investigations were carried out with a Philips EM400T transmission electron microscope operated at 120 kV. Electrochemical measure-

Table I. Various aqueous solutions used in the experiments (see text)

		Composition per liter
Α	Electroless Ni	30g NiCl <sub>2</sub> · 6H <sub>2</sub> O, 10g NaH <sub>2</sub> PO <sub>2</sub> · H <sub>2</sub> O, 30g glycine
В	Electroless Ni	$(pH = 3.8, 95^{\circ}C)$ Shipley Niposit 468 solution $(pH = 7, 65^{\circ}C)$ which utilizes di- methylamine borane as reducing
с	Electroless Cu	agent 10g CuSO <sub>4</sub> · 5H <sub>2</sub> O, 50g Rochelle salt, 10g NaOH, 25 ml conc. HCHO
D	Electroless Cu	(37%) (pH = 13.4, 25°C) 10g CuSO <sub>4</sub> · 5H <sub>2</sub> O, 32.6g Na <sub>4</sub> EDTA · 4H <sub>2</sub> O, 4.8g NaOH, 7.5
E	Electroless Au	ml conc. HCHO ( $pH = 13.2, 50^{\circ}$ C) 1.44g KAu(CN) <sub>2</sub> , 6.5g KCN, 8g NaOH, 10.8g KBH <sub>4</sub> ( $pH = 13.3, 70^{\circ}$ C)
F G	Pd photodeposition Sn sensitization	10  C/ $10 \text{ PdCl}_2, 10 \text{ ml conc. HCl (37\%)}$ $100 \text{ mg SnCl}_2 \cdot 2\text{H}_2\text{O}, 0.1 \text{ ml conc.}$ HCl
H I J K	Ag activation Pd activation O <sub>2</sub> photoreduction O <sub>2</sub> reduction	Ig AgNO <sub>3</sub> 1g PdCl <sub>2</sub> , 3.5 ml conc. HCl 6.5g KCN, 8g NaOH 4.8g NaOH

## **Results and Discussion**

Experimental examples of size effect.—Sn-Pd nuclei on glass.—The surface of a thin tapering glass rod was uniformly covered with electrocatalytic Sn-Pd nuclei using the Sn-Pd activation procedure. After a 1h immersion of the activated rod in an electroless Ni solution (A) a NiP layer was deposited only on that part of the rod with a diameter (d) larger than  $\approx 200 \ \mu m$  (13) (Fig. 1a). A critical diameter of  $\approx 200 \ \mu m$  below which NiP metallization did not occur was also found when activated glass fibers with various diameters were immersed in solution A.

Cu nuclei on  $TiO_2$ .—Isolated circular Cu spots with a diameter of  $\approx 13 \,\mu\text{m}$  were photodeposited from an electroless Cu solution (C or D) on a TiO<sub>2</sub> film on glass by illumination with a focused laser beam at low light intensity. After illumination the spots showed autocatalytic behavior only if the illumination time ( $\Delta t$ ) was longer than a critical value, say 1s (12). However, the autocatalytic growth of these isolated spots ceased after a short time and from that moment the spots remained stable in the solution. On the other hand, 36 Cu spots (each with  $\Delta t = 1$ s) deposited close together did show pertinent autocatalytic behavior after photodeposition (Fig. 1b).

Pd nuclei on  $TiO_2$ .—Circular Pd spots at relatively large mutual distances and with different diameters (d) and illumination times ( $\Delta t$ ) were photodeposited on a TiO<sub>2</sub> film on a glass plate in solution F (7) (Fig. 1c). In this experiment UV illuminations at low light intensity were carried out by imaging uniformly illuminated circular apertures with various sizes on the plate. Thus the amount of photodeposited Pd was homogeneously distributed within the spot and was proportional to the amount of surface area of the spot. When the plate was subsequently immersed in an electroless solution (Ni, Cu, or Au), metal deposition occurred



Fig. 1. Experimental configurations of patterns of nuclei: (a) thin tapering glass rod; (b) circular Cu spots on a TiO<sub>2</sub> film; (c) circular Pd spots on a TiO<sub>2</sub> film; only spots denoted by ● initiated electroless metal deposition.

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Fig. 2. (a) Linear  $O_2$  diffusion to a large activated area. (b) Linear and nonlinear  $O_2$  diffusion to a small pattern of nuclei.

only on Pd spots with a large diameter and/or a long illumination time. Figure 1c gives an example of the results when solution C was used, but the results in solutions A, B, D, and E were similar.

In the case of electroless Ni deposition from solution B the above experiment was repeated but now dissolved oxygen was purged from the solution by  $N_2$  bubbling. Compared with the experiment without  $N_2$  bubbling, Pd spots with relatively smaller diameters and/or shorter illumination times initiated electroless Ni deposition.

Subsequently, TEM observations of various Pd spots deposited on  $TiO_2/Si_3N_4$  specimens were performed to investigate the behavior of the Pd nuclei in the electroless solutions (B-E). It appeared that the size and morphology of Pd nuclei in nonactive spots did not change during their residence in an electroless Ni (B) or Cu solution (C or D) (7, 8). Pd nuclei in nonactive spots for electroless Au deposition completely dissolved in solution E. TEM investigations on the initial stages of electroless metal deposition on active Pd spots will shortly be published.

*Model.*—The following model considers electrocatalytic metal nuclei which are uniformly deposited in a disk with radius r on a dielectric substrate. The factor R is defined as the ratio of the electrocatalytic surface area of the nuclei and the geometric area. At time t = 0 the nuclei are immersed in an unstirred alkaline electroless solution. Apart from other species, the solution contains a reducing agent (Red), complexed metal ions  $[(M^{n+})_c]$  and dissolved oxygen.

At relatively large surfaces it suffices to consider mass transport and kinetics of two partial reactions, *i.e.*, anodic oxidation of Red (reaction [1]) and cathodic reduction of  $(M^{n+})_c$  (reaction [2]). However, when the patterns of nuclei are small it is necessary to consider  $O_2$  reduction (reaction [3]) as well, since the nonlinear diffusion flux of dissolved  $O_2$  to small single patterns is much larger than the linear  $O_2$ diffusion flux to large areas (Fig. 2). Thus the following current densities (*j*) of three partial reactions at the disk are considered<sup>1</sup>

j(Red) : Red  $\rightarrow$  Ox + me [1]

$$j(\mathbf{M}^{n+})$$
 :  $(\mathbf{M}^{n+})_{c} + ne \rightarrow \mathbf{M}$  [2]

$$j(O_2)$$
 :  $O_2 + 2H_2O + 4e \rightarrow 4 OH^-$  [3]

The value of the open-circuit potential of the nuclei ( $V_{oc}$ ) determines whether metal deposition occurs. Generally it can be stated that, at t = 0, the surface of the nuclei is covered with oxygen species (O, OH). Consequently, the value of  $V_{oc}$  will be in the range (+0.7, +0.9V) vs. the reversible hydrogen electrode (RHE), which is positive with respect to the reversible redox potential of reaction [2] ( $V((M^{n+})_{o}/M)$ ). This is indicated by a commonly observed induction time at the start of electroless metal deposition and more directly by open-circuit potential transients at bulk electrodes (14, 15). Thus from t = 0 reactions [1] and [3] occur simultaneously at the surface of the nuclei. The competition between these two reactions, *i.e.*, the relative

<sup>1</sup>The exact stoichiometry of reaction [3] is not important here;  $O_2$  reduction is written as a four-electron reaction, but a two-electron reaction is also possible.

values of j(Red) and  $j(O_2)$ , will determine whether  $V_{\text{oc}}$  is shifted to a sufficiently negative value at which metal deposition is initiated. Assuming that there is no overpotential or underpotential for the deposition of the first monolayers of metal M on the small (foreign) metal nuclei, this occurs only if  $V_{\text{oc}}$  becomes negative with respect to  $V((\mathbf{M}^{n+})_c/\mathbf{M})$ .

Generally, the kinetically determined current density of reaction [1] at bulk electrocatalytic metals is lower than that of reaction [3]. The former is commonly in the range 1-10 mA/cm<sup>2</sup> metal area (16) while the latter can be higher than 10 mA/cm<sup>2</sup> (17) (*e.g.*, on Group VIII metals but also on Au at pH > 13). Both depend, among other factors, on the temperature, pH, specific metal and, more important, the potential V. Analogous to electrocatalysis at bulk metals, it is now assumed that j(Red) is determined by kinetics in the whole range of potentials at which anodic oxidation of Red at bulk metals occurs (16), while  $j(O_2)$  is determined by diffusion at sufficiently negative potentials.

Thus j(Red) is determined by the amount of electrocatalytic surface area of the nuclei, *i.e.*,  $j(\text{Red}) = k \cdot R$ , where k is the kinetically determined current density of reaction [1] at the nuclei. Two typical values of j(Red), obtained by taking  $k = 2 \text{ mA/cm}^2$ , R = 0.1 and R = 0.5, are indicated in Fig. 3.

The maximum possible value of  $j(O_2)$  ( $j_m(O_2)$ ) is evaluated by considering complete mass-transport-controlled O<sub>2</sub> reduction at a microdisk from t = 0 (18)

$$j_{\rm m}({\rm O}_2) = 4\mathbf{F}C\left(\left(\frac{{\rm D}}{\pi t}\right)^{1/2} + \frac{4{\rm D}}{\pi r}\right) \qquad [4]$$

Figure 3 shows a logarithmic plot of  $j_m(O_2)$  vs. t for various values of r,  $D = 2 \times 10^{-5}$  cm<sup>2</sup>/s and  $C = 2.7 \times 10^{-7}$  mol/cm<sup>3</sup> (O<sub>2</sub> concentration in air-saturated water at 25°C). Clearly, for small values of r steady-state nonlinear diffusion predominates over time-dependent linear diffusion at relatively short times. Comparing values of  $j_m(O_2)$  (Fig. 3) with diffusion-controlled current densities for O<sub>2</sub> reduction at rotating metal disk electrodes, it is concluded that O2 reduction at the microdisk at sufficiently negative potentials will be controlled by nonlinear O<sub>2</sub> diffusion for a wide range of values of  $r (\approx 1 \, \mu m < r < \approx 1 \, mm)$ . If r becomes larger than  $\approx 1$  mm, O<sub>2</sub> mass transport will be determined by the diffusion layer thickness, while kinetic factors are expected to limit the rate of  $O_2$  reduction when r becomes smaller than  $\approx 1 \,\mu\text{m}$ . In conclusion,  $j(O_2)$  may become appreciably larger than j(Red) for small values of r.

Experimental justification of assumptions.—Uniform distribution of nuclei.—The uniform distribution of small electrocatalytic metal nuclei on a dielectric substrate is illustrated by characteristic TEM observations of metal nuclei deposited according to two different procedures (Fig. 4). Figure 4a shows crystalline Pd metal nuclei with sizes in the 2.0-4.0 nm range and a surface number density of  $\approx 3 \times 10^{11}$ /cm<sup>2</sup>, which were photodeposited on a thin TiO<sub>2</sub>/ Si<sub>3</sub>N<sub>4</sub> film from solution F at a relatively high light inten-



Fig. 3. Logarithmic plot of  $j_m(O_2)$  vs. t for different values of r (Eq. [4]). Two characteristic values of j(Red) are also indicated.

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Fig. 4. TEM bright-field images which show the uniform distribution of small nuclei. (a) Photodeposited Pd nuclei on a thin polycrystalline TiO<sub>2</sub> film which is supported by a thin amorphous Si<sub>3</sub>N<sub>4</sub> film; (b) deposited Sn-Pd nuclei on a thin amorphous SiO<sub>2</sub> film.

sity (7, 8). The densities of photodeposited Pd nuclei in the experiments mentioned above were lower than  $3 \times 10^{11}$ / cm<sup>2</sup> due to the lower light intensities used (7).

Figure 4b shows Sn-Pd nuclei with sizes in the 1.0-4.0 nm range and a density of  $\approx 10^{12}/\text{cm}^2$ . These were deposited on a thin amorphous SiO<sub>2</sub> film according to the Sn-Pd activation procedure which was used for clean glass substrates. By dark-field imaging and electron diffraction, it was shown that the nuclei are crystalline but they do not have the structure of bulk Sn or bulk Pd metal. Most probably, they consist of a metal alloy of Sn and Pd.

For illustration, from Fig. 4a and b the values of the factor *R* are roughly estimated to be 0.05 and 0.1, respectively.

Nonlinear diffusion of oxygen.—The possibility of a large nonlinear diffusion flux of dissolved oxygen to small electrode areas is illustrated by electrochemical measurements of mass-transport-controlled  $O_2$  reduction at lightgenerated microdisks on a p-GaAs electrode (19) and at Pd microcylinder electrodes.

 $O_2$  reduction was spatially controlled by imaging a uniformly illuminated circular aperture on a p-GaAs electrode in solution J ( $O_2$  saturated). At the potential of the electrode (-1.2  $V_{SCE}$ ) the dark current was negligible. It was found that the current density from time t = 0, when illumination was started, is given by Eq. [4], thus indicating complete mass-transport controlled  $O_2$  photoreduction at the light-generated microdisk. By measuring the steady-state current as a function of the spherical  $O_2$  diffusion flux is proportional to  $r^{-1}$  (see Fig. 5a).

Figure 5b shows current-density potential curves of  $O_2$ reduction at Pd microcylinder electrodes with various diameters in solution K. Clearly, the limiting current density due to cylindrical  $O_2$  diffusion increases when the diameter of the Pd wire decreases. From potentiostatic current-



Fig. 5. Electrochemical measurements of O<sub>2</sub> reduction at microelectrodes. (a, left) Logarithmic plot of the steady-state O<sub>2</sub> photoreduction current density  $(j_i)$  vs. the radius of a light-generated microdisk on a p-GaAs electrode in solution J at  $-1.2 V_{SEC}$ . (b, right) Current-density potential curves for O<sub>2</sub> reduction at Pd microcylinder electrodes with various diameters in solution K. Scan velocity: 10 mV/s.

time measurements at sufficiently negative potentials (V <  $-0.3~V_{\rm SCE}$ ) it appeared that the measured quasi-steady-state current densities are approximately equal to the limiting current densities shown in Fig. 5b.

Mixed potential theory.—Induction time.—The size effect will now be discussed by introducing the concept of the mixed potential (20) in the above model of electroless deposition on an isolated circular disk. Figure 6 shows schematically characteristic polarization curves of j(Red),  $j(M^{n+})$ , and  $j(O_2)$  for a microdisk with various sizes  $(r < 500 \ \mu\text{m}; \text{Fig. 6a)}$  and for a large disk  $(r > 5 \ \text{mm}, \text{Fig. 6b)}$ . The steady-state mixed potential  $(V_{\text{M}})$ , at which j(Red) equals  $j(M^{n+}) + j(O_2)$ , is also indicated. First we consider the establishment of this potential.

As discussed previously, the initial electrocatalytic activity of the nuclei for reactions [1] and [3] and the supply of oxygen generally determine whether  $V_{oc}$  is shifted from the initial value in the range [+0.7, +0.9V] vs. RHE to a value which is negative with respect to  $V((M^{n+})_c/M)$ . The essential condition, necessary to make this negative potential shift possible, is that j(Red) is larger than  $j(O_2)$ . The time after t = 0 which it takes to accomplish the shift is known as the induction time in electroless metallization.

The initial supply of oxygen to the nuclei is relatively high for both a large (r > 5 mm) and a small  $(r < 500 \text{ }\mu\text{m})$ spot (see Fig. 3). The supply of O<sub>2</sub> to a large spot may decrease significantly from t = 0 due to O<sub>2</sub> reduction at the nuclei. On the contrary, the supply of O<sub>2</sub> to a small spot can be maintained at a high level due to the large nonlinear O<sub>2</sub> diffusion flux (Fig. 3). Thus it can be understood that, at a large spot,  $j(O_2)$  can eventually become smaller than j(Red), while this becomes increasingly unlikely when the spot becomes smaller.

The negative shift of the open-circuit potential of bulk electrodes occurs mostly rather abruptly and is probably associated with the removal of surface oxygen species. This indicates the importance of these species in determining the initial electrocatalytic activity of the nuclei for reaction [1] and/or [3]. The initial *j*(Red), and consequently the length of the induction time, are possibly determined by the rate of dissociative chemisorption of Red at the surface of the nuclei. The exact origin of the induction time and the mutual dependence of reactions [1] and [3] are currently being investigated.

*Oxygen-diffusion-size effect.*—Figure 6b represents the traditional approach of the mixed potential theory to electroless metal deposition on a relatively large substrate in an unstirred solution.  $j(O_2)$  represents mainly the linear  $O_2$  diffusion flux to the substrate. The maximum steady-state value of  $j(O_2)$  is determined by the diffusion layer thickness and is only approximately 50  $\mu$ A/cm<sup>2</sup> for an unstirred solution. Since j(Red) and  $j(M^{n+})$  are usually much larger than  $j(O_2)$ , the latter is often neglected.

Figure 6a shows the principal cause of the so-called oxygen-diffusion-size (ODS) effect in electroless metallization. If the size of the spot is smaller than some critical value,  $j(O_2)$  is larger than j(Red), and  $V_{oc}$  cannot be shifted to a potential which is negative with respect to  $V((\mathbf{M}^{n+})_{o}/\mathbf{M})$ . In this case the nuclei will either dissolve or remain stable, depending on the composition of the electroless solution.

Dissolution may occur if the solution contains a strong complexing agent for the ions of the metal nuclei. The dissolution can be described by an electroless corrosion mechanism at the nuclei, the cathodic process being reaction [3] and the anodic processes being oxidation (and complexation) of the metal and reaction [1]. If the metal nuclei cannot dissolve (see Fig. 6a)  $V_{oc}$  will be fixed, by reactions [1] and [3], at an anodic value in the range [+0.7, +0.9V] vs. RHE where the surface is passivated by species like MeOH (e.g., if Me = Pd) or Me<sub>2</sub>O (e.g., if Me = Cu). These species may already be present at t = 0 and can be formed by O<sub>2</sub> reduction and a partial anodic reaction

$$\begin{split} \mathbf{Me} + \mathbf{OH}^- &\rightarrow \mathbf{MeOH} + e \\ \mathbf{2Me} + 2 \ \mathbf{OH}^- &\rightarrow \mathbf{Me_2O} + \mathbf{H_2O} + 2e \end{split}$$

Since the cyanide ion is a much stronger complexing agent for Pd ions than EDTA or tartrate, it can qualitatively be understood that photodeposited Pd nuclei in nonactive Pd spots on a TiO<sub>2</sub> film are dissolved in an electroless Au solution while their morphology does not change in an electroless Cu solution (see section on Pd nuclei on TiO<sub>2</sub>). The Pd nuclei are also expected to dissolve in clean aqueous solutions that are free from (oxidizable) organic impurities, since then  $V_{oc}$  will be determined by O<sub>2</sub> reduction and Pd dissolution (21).

The ODS effect is not only observed when the spot size is decreased but also when the factor R is decreased. When R decreases j(Red) decreases, while  $j(O_2)$  is nearly constant since reaction [3] is assumed to be diffusion controlled. This qualitatively explains why in the experiment described in the section on Pd nuclei on TiO<sub>2</sub>, at a constant size of the Pd spot, electroless metallization does not occur when the illumination time is shorter than a critical value. Obviously, the value of R is decreased when the illumination time is decreased.



Fig. 6. Schematic polarization curves of reactions [1], [2], and [3] at a small ( $r < 500 \ \mu$ m) disk with different radii (a, left) and at a large ( $r > 5 \ m$ m) disk (b, right). V<sub>M</sub> is the steady-state mixed potential at which j(Red) equals j(M<sup>n+</sup>) + j(O<sub>2</sub>).

Extinction of deposition.—The ODS effect also explains the inhibition of electroless metal deposition on small spots that were initially autocatalytic. Electroless deposition is started since the original metal nuclei have a relatively large electrocatalytic activity for reaction [1]. However, when the metal nuclei are completely covered by the electroless deposit, the latter cannot continue the autocatalytic growth due to the relatively increased contribution of reaction [3].

For example, this phenomenon may occur in the electroless Cu deposition on photodeposited Pd or Cu spots on TiO<sub>2</sub> films (see section on experimental examples of size effect). In the latter case it was shown by HREM and in situ EXAFS measurements that spots, photodeposited directly from an electroless Cu solution (C or D), contain Cu particles if the illumination time is sufficiently long (12). The autocatalytic growth of these spots ceased after a short time due to the formation of copper oxide particles. It is well known that electroless Cu deposition is retarded or even completely inhibited when the concentration of  $O_2$ in the solution is increased [e.g., Ref. (22)].

High density of patterns.—So far, the ODS effect has been discussed for isolated spots. It was experimentally confirmed (section on Cu nuclei on TiO<sub>2</sub>) that the ODS effect becomes less important when the density of small patterns of electrocatalytic nuclei on a substrate becomes greater. The reason for this is that the O2 diffusion zones associated with the patterns overlap more and more when the distance between neighboring patterns become smaller. This implies that the current density of reaction [3] at these patterns will decrease since the supply of  $O_2$  is distributed over a large surface area. At high densities of patterns the total supply of O2 is determined by linear diffusion to an effectively planar substrate and the ODS effect may not be noticed anymore.

Practical solutions.-The following practical solutions are proposed to circumvent the ODS effect when small patterns of nuclei are to be intensified by electroless metal deposition:

1. Oxygen removal from the solution by purging with an inert gas.

2. An increase of the temperature which increases enormously the relative rate of reaction [1] with respect to reaction [3] (16).

3. Use of a more powerful reducing agent or a change in the composition of the solution so that j(Red) is increased, particularly at potentials in the range [+0.7, +0.9V] vs. RHE

4. The development of (acidic) electroless solutions in which oxygen reduction is kinetically and/or thermodynamically less favored at the plating potential  $V_{\rm M}$  (e.g., for  $V_{\rm M} > 0.9 V_{\rm RHE}$ ; cf. physical developers).

However, these solutions have the disadvantage that either the electroless solution becomes kinetically less stable and/or that spontaneous nonselective metal deposition on the substrate is encouraged.

The stabilization of electroless solutions.-Electroless solutions are often stabilized for longer operating times by the use of very small amounts of poisoning additives [23]. The enhanced stability can be explained by the same principle as described for the ODS effect. By strongly adsorbing on the metal surface the poisoning species cause a decrease in the plating rate. In general, the rate of adsorption will be determined by the rate of mass transport. Consequently, the autocatalytic deposition on large can still proceed at an appreciable rate, since the linear diffusion flux of the poisoning species to the metal surface is relatively small. Moreover, the surface is continuously renewed by metal deposition at a rate much higher than the adsorption rate of the poison. This prevents complete poisoning of the surface. However, the spontaneous decomposition of the solution, by homogeneous nucleation and subsequent autocatalytic growth of the nuclei formed, is suppressed by a large spherical diffusion flux of the poisoning species to

the small nuclei. Thus, very small concentrations of stabilizers (ppm range) are usually sufficient to inhibit the growth of nuclei in the bulk of the solution effectively. This effect has been confirmed by Rozenblyum et al. [24]. They found that the poisoning concentration of a stabilizer, such as thiosulfate in an electroless nickel solution, was lowered when the radius of curvature of the metal surface was reduced.

## Conclusion

It has been shown, both by theory and experiment, that there is a limit to the size of isolated electrocatalytic patterns below which electroless metal deposition does not occur. The principal cause of this inhibition effect is the effectively enhanced supply of oxygen to small patterns due to nonlinear diffusion of dissolved oxygen.

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