Selective Metallization of Silicon Surfaces
The Adsorption of Sterically Stabilized Palladium Particles on H-Terminated Si(100), Si₃N₄, and SiO₂

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ABSTRACT

The adsorption of nanometer-sized, palladium-phosphorus particles (Pd₄₈ glam P₄₈) onto Si₃N₄, SiO₂, and H-terminated Si(100) surfaces is described. These colloidal particles were prepared in aqueous solution by the reduction of Pd²⁺ with hypophosphite in the presence of polyvinylpyrrolidone (PVP). The sterically stabilized particles catalyze Ni deposition from an electroless solution. High resolution electron microscopy shows that the particle size decreases with increasing PVP concentration in the sol. Several monocrystalline domains were observed in all particle samples. The surface affinity of Pd particles, covered with PVP, and of “free” PVP molecules (i.e., not associated with Pd particles) depends strongly on the type of surface. The large differences in Pd coverage between different types of surface (e.g., Si₃N₄ and SiO₂) offer interesting possibilities for novel pattern-wise electroless metallization procedures.

Introduction

The electroless metallization of semiconductors and non-conducting materials is of considerable industrial importance. Electroless deposition (e.g., Ni) requires a catalytically active surface. An interesting activation procedure involves the adsorption of colloidal Pd particles on the surface to be plated. Differences in surface coverage of catalyst particles on different types of surface offer interesting possibilities for pattern-wise electroless metallization. An example of this type of approach is the selective metallization of indium tin oxide (ITO) patterns on glass substrates. It was shown that Pd particles, stabilized with polyvinylalcohol, adsorb on ITO but not on glass. An electroless metal layer could, therefore, be selectively grown on the ITO pattern. The ultimate goal is to produce Pd particles, stabilized with water soluble polymers, with a high and specific affinity for a particular type of surface, enabling selective metallization.

In a previous paper, the adsorption on H-terminated Si(100) single-crystal surfaces of nanometer-sized Pd particles, sterically stabilized with polyvinylpyrrolidone (PVP), was reported. These colloidal Pd particles were prepared in aqueous solution by the reduction of Pd²⁺ ions with hypophosphite in the presence of PVP. We described the strong influence of the PVP concentration on the Pd particle size and the Pd coverage of the Si substrate. On Si surfaces, a competitive adsorption was observed between Pd particles, stabilized with PVP, and “free” PVP molecules (i.e., not associated with Pd particles). No significant influence of the molecular weight of the PVP on the adsorption was observed. In addition, we found no adsorption of Pd particles on oxidized Si surfaces.

In the present work, we consider how the chemical nature of the surface influences the adsorption of colloidal Pd particles. We studied Si₃N₄ and SiO₂ surfaces and compare the results with those previously obtained on H-terminated Si(100). The adsorption process is discussed in terms of particle-substrate and polymer-substrate interaction. A relation can be expected between the size and the polymer coverage of the metal particles and their affinity for a particular surface. Therefore, the size and atomic structure of Pd particles, prepared in the presence of different concentrations of PVP, were studied in detail by high resolution electron microscopy (HREM). Possible methods of pattern-wise metallization are discussed at the end of the paper.

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Experimental

All chemicals used were of analytical grade, and the solutions were prepared with deionized water. A 0.056M palladium chloride solution was prepared by dissolving 1.00 g PdCl₂ in 35 ml concentrated hydrochloric acid (37%, Merck) and making it up to 100 ml with water. PVP samples with various (average) molecular weights (M_avg) were used in this study (M_avg: 10,000, 40,000 from Fluka, and 360,000 from Janssen; stock solution: 9.11 g PVP/liter). Sodium hypophosphite was used as the reducing agent (0.48M solution).

The silicon nitride samples consisted of 120 nm Si₃N₄ grown by chemical vapor deposition on Si(100) wafers provided with 50 nm SiO₂. The silicon dioxide samples were 100 nm thick, thermally grown at 1000°C in oxygen, on p-type Si(100) wafers (20 cm), Wacker-Chemitronic GmbH, Germany. The Si single-crystal wafers were (100)-oriented samples (boron doped, 20 to 30 Ω cm) obtained from Shinetsu. The wafers were cut into pieces of 15 × 15 mm² and ultrasonically cleaned in ethanol. To obtain a fresh surface, the SiO₂ and Si₃N₄ wafers were etched for 0.5 and 2 min, respectively, in an aqueous NH₄F-HF solution (pH 6), and rinsed under running water. The Si₃N₄ layers etch slowly in the NH₄F-HF solution (~1 min/m). The SiO₂ layers etch relatively fast in this solution (~30 min/m). After this treatment, both the Si₃N₄ and SiO₂ surfaces were hydrophilic (water contact angle <90°). The native oxide on the Si surfaces was removed by etching for about 1 min in the NH₄F-HF solution. The etch rate of Si in this solution is extremely low (<0.1 nm/min). After etching, the Si surface was hydrophobic (water contact angle ~78°) and H terminated.

Palladium sols containing Pd, PVP, and hypophosphite in varying concentration ratios were used. First, a solution containing the required amounts of Pd and PVP was prepared. While the (air-saturated) solution was stirred, a given volume of the hypophosphite solution was added. After an "induction period" of 3 to 5 min, the color of the solution (pH 1.2) turned from yellow to transparent brown due to the formation of metallic Pd. No corrosion of the particles occurred because the Pd sol is saturated with dissolved hydrogen after formation. The sols were found to be colloid-chemically stable during adsorption of the particles on the substrate. In general, 10 min after the addition of the hypophosphite solution, a cleaned and etched Si₃N₄, SiO₂, or Si sample was introduced into the Pd sol immediately after the rinsing step. Adsorption of the Pd particles was allowed to occur, in general, for a period of 5 min. Afterward, the surface was briefly rinsed under running...
water and dried in air. In all cases, adsorption caused no noticeable depletion of Pd from the solution. All experiments were performed at room temperature.

The Pd surface coverage (ΓPd) of the samples was measured by x-ray fluorescence spectroscopy (XRF) using a Philips PW 1404 spectrometer. The detection limit for Pd on the substrates was 0.02 × 10¹⁵ Pd atoms/cm². Samples for HREM work were 13 nm thick Si₃N₄ membranes prepared by preferential local etching of an Si(100) wafer support in a KOH-H₂O-isopropanol solution. The Pd particles, adsorbed onto these thin Si₃N₄ membranes, were studied with a Philips CM30 transmission electron microscope operating at 250 keV.

In some experiments, an SiO₂ surface, covered with a PVP monolayer, was oxidized pattern-wise using a contact mask in a UV/ozone reactor (UV/ozone photoreactor, PR-100, UVP Inc.) for 10 min. After activation of the substrate in a colloidal Pd solution, an electroless Ni layer was grown by immersing the substrate for 1 min in an electroless Ni plating bath (Niposit 468, Shipley, Newton, MA) operated at 65°C. This procedure results in the formation of an Ni film (0.25% B) on the activated parts of the surface, with a growth rate of 7.5 μm/h.

Results

HREM images (75 × 75 nm²) of Pd particles adsorbed on Si₃N₄ membranes are shown in Fig. 1 (curves a-c). These are images of particles prepared in the presence of different concentrations of PVP (M_pvp: 10,000). A significant decrease in particle size with increasing PVP concentration is found. A transition from irregularly shaped to spherical particles is observed. It was found that at a PVP concentration of about 50 mg/liter (c_pvp = 8.46 × 10⁻⁴M, c_H₂PO₂⁻ = 1.56 × 10⁻²M), the particles reach their minimum size (~3 nm diam). Relatively monodispersed particles are shown in Fig. 1 (curve c, c_pvp = 114 mg/liter). In Fig. 2, a single 6 nm diam particle is shown; the atomic structure of the lattice is clearly resolved. In all particles, several monocrystalline domains were observed. In the case of Si(100), no preferential orientation of monocrystalline Pd particles with respect to the (100) surface was observed. The palladium and phosphorus content of these colloidal particles was measured by XRF after adsorption onto an H...
terminated Si surface. Figure 3 shows the phosphorus content of Pd particles adsorbed on Si to be 14 atom percent (a/o), independent of the PVP ($M_{pp}$: 10,000) concentration. No phosphorus was found on Si samples treated with a blank solution containing HCl, PVP, and hypophosphite.

The Pd surface coverage ($\Gamma_{pd}$) on Si$_3$N$_4$ was measured as a function of the adsorption time ($M_{pw}$: 10,000). Figure 4 shows that $\Gamma_{pd}$ increases rapidly and, within a minute, reaches an almost steady value which only slightly increases with time. In the experiments of Fig. 4, the Pd-covered Si$_3$N$_4$ surface was rinsed with air-saturated water between adsorption and XRF determination. Figure 5 (curve a) shows that $\Gamma_{pd}$ does not decrease for a rinsing time of up to 100 min. However, in (air-saturated) water containing HCl ($6.34 \times 10^{-2}$M), a significant decrease of $\Gamma_{pd}$ was found (Fig. 5, curve b). In Fig. 6, the Pd surface coverage is plotted against the Pd concentration in solution; the solutions were obtained by dilution of a more concentrated sol ($c_{pd} = 8.46 \times 10^{-4}$M, $c_{NaH_2PO_2} = 1.56 \times 10^{-2}$M, $c_{pp}$: 114 mg/liter, $M_{pp}$: 10,000) with an aqueous solution containing HCl ($6.34 \times 10^{-2}$M) and Na$_2$HPO$_2$ ($1.56 \times 10^{-2}$M) to keep the ionic strength and composition constant. An adsorption plateau is reached at very low Pd concentrations in the sol. The adsorption of Pd particles on Si$_3$N$_4$ was measured as a function of the PVP concentration ($M_{pp}$: 10,000). Figure 7 (curve a) shows a plot of $\Gamma_{pd}$ vs. the logarithm of the polymer concentration ($\log(c_{pp})$). A continuous decrease of the Pd surface coverage with increasing PVP concentration is found. Two roughly linear regions can be observed in Fig. 7 (curve a) with a sharp transition at around $c_{pp} = 50$ mg/liter. In the PVP concentration range of 50 to 1000 mg/liter, a slight decrease in $\Gamma_{pd}$ is observed. For comparison, the corresponding $\Gamma_{pd}$
Fig. 6. Pd coverage ($\Gamma_{pd}$) of Si$_3$N$_4$ as a function of the Pd concentration. $C_{pd}$ vs. $C_{p}$. The adsorption time was 5 min. $C_{p}$ vs. $C_{pd}$ = 1.35 x $10^{-5}$ (mg PVP/mol Pd), $M_{p}$ = 10,000.

vs. log $C_{p}$ for an H terminated Si surface is also plotted (Fig. 7, curve b). For the Si surface, the same transition at around $C_{p}$ = 50 mg/liter was observed.

The adsorption on SiO$_2$ of Pd particles, stabilized with PVP ($M_{p}$ = 10,000, 40,000, and 360,000), was measured as a function of the PVP concentration in the sol (Fig. 8, curves a-c). For the three molecular weights studied, $\Gamma_{pd}$ is low over the entire PVP concentration range ($\Gamma_{pd}$ < 0.8 x $10^{-5}$ Pd atom/cm$^2$), especially for the low molecular weight PVP. A maximum in $\Gamma_{pd}$ was observed, after which $\Gamma_{pd}$ decreases to very low values. For the experiment of Fig. 9 (curve a), the SiO$_2$ surface was first immersed for 5 min in a solution containing 1140 mg PVP/liter ($M_{p}$ = 10,000), 1.56 x $10^{-2}$M NaH$_2$PO$_2$, and 6.34 x $10^{-2}$M HCl before adsorption of colloidal Pd. For comparison, the adsorption of the corresponding colloidal Pd onto bare SiO$_2$ is shown in Fig. 9 (curve b). Palladium adsorption strongly increases after pretreating the surface with PVP, particularly for sols containing small amounts of polymer.

Discussion

In the present work, the adsorption of nanometer-sized Pd particles on Si$_3$N$_4$ and SiO$_2$ surfaces was studied. Results for H-terminated Si(100) were discussed in an earlier paper. From that study we concluded that a combination of particle-substrate and polymer-substrate interactions determines the adsorption of colloidal Pd. In general, a combination of chemical and electrostatic particle-substrate interactions are expected to play a role in the adsorption process. These effects are discussed here in some detail.

An increase in the concentration of PVP in the sol decreases the Pd particle size (Fig. 1, curves a-c). In our previ-
The fact that Pd adsorption still increases slowly over longer periods of time is presumably due to a relatively slow reorganization in the adsorbed phase, allowing for the creation of some additional adsorption sites. After the initial fast increase, the further increase in $I_{Fp}$ is, in general, less than $0.2 \times 10^{12} \text{ Pd atom/cm}^2$. The same effect was already observed for the adsorption of colloidal Pd on H-terminated Si(100). The results in curve a of Fig. 5 illustrate that adsorption of Pd particles on Si$_3$N$_4$ surfaces is irreversible. No desorption occurred during rinsing with water. When Cl$^-$ ions are present, adsorbed Pd particles are slowly oxidized by dissolved oxygen (Fig. 5, curve b). This can be explained from the negative shift in equilibrium potential of the Pd(II)/Pd couple due to complexation of Pd with Cl$^-$ ions. This shift increases the driving force for oxidation by dissolved O$_2$.

In Fig. 7 the Pd surface coverage is plotted against the logarithm of the polymer concentration in the sol ($\log c_{PVP}$) for an Si$_3$N$_4$ and an H-terminated Si surface (curves a and b, respectively). For both types of surface, a continuous decrease of $I_{Fp}$ with increasing PVP concentration is observed. In previous work on H-terminated Si it was concluded that, up to the kink in curve b of Fig. 7 ($c_{PVP} \approx 50 \text{ mg/liter}$), the number density of adsorbed Pd particles is about constant while the size of the adsorbed Pd cores of the PVP covered mesoparticles decreases, resulting in a lower Pd surface coverage. The particle size becomes constant at $c_{PVP} \approx 50 \text{ mg/liter}$. After the kink, “free” PVP molecules (i.e., not associated with Pd particles) are considered to be present in the sol. Both Pd particles, covered with PVP, and free PVP are able to adsorb onto the Si surface. There is a competition between the adsorption of Pd particles and polymer molecules.

A remarkable difference in adsorption between Si$_3$N$_4$ and Si is observed. In the case of Si$_3$N$_4$, $I_{Fp}$ decreases only slowly with increasing $c_{PVP}$ after the kink (Fig. 7, curve a). In contrast, for Si, $I_{Fp}$ decreases strongly with increasing polymer concentration (Fig. 7, curve b). For $c_{PVP} \approx 1200 \text{ mg/liter}$, the Si surface is completely blocked by PVP ($I_{Fp} = 0$). At this PVP concentration, the Pd surface coverage on Si$_3$N$_4$ is still high ($I_{Fp} = 1.6 \times 10^{12} \text{ Pd atom/cm}^2$). No or only slight desorption of Pd particles occurred when an Si or an Si$_3$N$_4$ surface, covered with Pd particles, was immersed in a PVP solution, containing 9.11 g PVP/liter over a long period (1 to 24 h). On the other hand, preadsorbed Pd particles on Si$_3$N$_4$ could be displaced instantaneously by Pd particles. Preadsorbed Pd on Si could be displaced only over a longer period (~30 min). Obviously, the affinity of Pd particles for Si$_3$N$_4$ is much higher than that of PVP molecules for this surface. The strong affinity of the Pd particles for Si$_3$N$_4$ may be explained by assuming H$^+$ coupling to surface nitrogen atoms giving rise to a positively charged surface. Pd particles are expected to have a negative charge due to specific adsorption of Cl$^-$ ions. In spite of the presence of the steric layer, interaction between particles and the surface seems to occur. In the case of H-terminated Si, the observations point toward a strong affinity of both Pd particles and PVP for this surface. From $c_{PVP} < 50 \text{ mg/liter}$, the case where no free polymer is present in the sol, similar curves are expected for Si and Si$_3$N$_4$. The difference in this concentration range is possibly due to a difference in conformation between adsorbed Pd particles, covered with PVP, on Si and Si$_3$N$_4$. The higher affinity of PVP for Si suggests attraction and deformation of the steric layer surrounding the particle upon adsorption. This should increase the occupied area per particle on Si, giving rise to a lower Pd surface coverage.

The results in curve a of Fig. 8 illustrate that the Pd surface coverage on SiO$_2$ is very low over the entire PVP concentration range studied ($M_{PVP} = 10,000$). For the case in which no free PVP molecules are considered to be present in the sol ($c_{PVP} < 50 \text{ mg/liter}$), Pd adsorption does not take place. In addition, no Pd was detected on SiO$_2$, surfaces for...
Pd sols prepared in the absence of PVP. The measurements suggest that the low molecular weight PVP molecules, absorbed on Pd particles, have no “free” tails which can interact with the SiO₂ substrate. It is known that Pd has a strong interaction with SiO₂. The observations suggest a compact structure of the PVP layer around the metal particles. It is reasonable to assume that the thickness of the steric layer of the Pd particle depends on the PVP to Pd ratio of the sol. For \( C_{\text{PVP}} < 50 \text{ mg/liter} \), the Pd particles have an incomplete and thin steric layer. For these particles, electrostatic repulsion between the particle and the substrate seems to be important. The surface of the Pd particle is expected to be negatively charged due to the specific adsorption of Cl⁻ ions. The SiO₂ surface may have a slightly negative charge because of the acidic character of SiO₂.

In the case of low molecular weight PVP (Fig. 8, curve a), particle adsorption occurs on SiO₂ when \( C_{\text{PVP}} > 50 \text{ mg/liter} \) resulting in low Pd coverages (\( \Gamma_{\text{Pd}} \approx 0.2 \times 10^{18} \text{ Pd atom/cm}^2 \)). At high PVP concentration a well-developed steric layer is formed. Pd particles prepared at high PVP concentration are expected to have a more PVP-like character and a corresponding higher affinity for SiO₂ compared with Pd particles prepared with a low PVP concentration. This explains the adsorption of both PVP and Pd at \( C_{\text{PVP}} > 50 \text{ mg/liter} \): In the case of higher molecular weight PVP (Fig. 8, curves b and c), “free” PVP tails on the particle are more likely. These particles or multiparticle complexes are able to adsorb on SiO₂.

The presence of a preadsorbed PVP layer on SiO₂ has a considerable influence on the subsequent adsorption of colloidal Pd (Fig. 9). Adsorption of particles occurs when \( C_{\text{PVP}} < 50 \text{ mg/liter} \), the range in which the particles are assumed to have an incomplete steric PVP layer (the situation before the kink in Fig. 7). Interaction of free PVP tails present on the SiO₂ surface, with the particle surface is then possible. When the particle has a fully developed steric layer, \( \Gamma_{\text{Pd}} \) becomes very low (\( \Gamma_{\text{Pd}} < 0.4 \times 10^{15} \text{ Pd atom/cm}^2 \)), and interaction is no longer possible.

The adsorption results as presented in Fig. 9 can be successively employed to produce metal patterns. One procedure is schematically depicted in Fig. 10. First, a clean SiO₂ surface is modified by adsorption of PVP. Subsequently, a metal contact mask is placed on the surface. In a UV/ozone reactor the PVP is oxidized according to the pattern in the mask. The surface, without the mask, is then immersed in a Pd sol, prepared in the absence of PVP. Particles in such a sol only adsorb on the PVP covered SiO₂, while the UV/ozone treated parts of the surface remain uncovered. Subsequent electroless Ni metallization leads to the growth of an Ni layer on the activated parts of the surface (Fig. 11). Metal patterns can, in principle, be made on Si by defining an SiO₂ pattern on the Si, followed by selective adsorption of colloidal Pd. Adsorption occurs on the unoxidized surface only. Subsequent electroless metallization and oxide etching yields a metal pattern on Si. Snow et al. showed that it is possible to “write” oxide lines (~100 nm width) on an H-passivated Si(100) surface with a scanning tunneling microscope (STM) operating in air. Using the large difference in Pd surface coverage on SiO₂ and H-terminated Si, electroless metal patterns could be selectively grown on the unoxidized parts of the surface. This offers interesting possibilities for the fabrication of metal nanostructures on Si using STM.

In forthcoming contributions, the adsorption of Pd particles and the polymer on various substrates, studied in situ with reflectometry, will be discussed. The catalytic properties of PVP-stabilized Pd particles on Si surfaces for electroless Ni deposition are currently being studied.

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