Photoelectrochemical Deposition of Nickel onto TiO_2 Particles. Formation of Nickel Patterns without Resists

Shinya MORISHITA* and Ken-ichi SUZUKI
Toyota Central Research and Development Laboratories, Inc., 41-1, Yokomichi, Nagakute, Aichi 480-11
(Received August 30, 1993)

In the presence of citric acid, the photoelectrochemical deposition of nickel onto TiO_2-sol particles was observed due to the quantum size effect. Selective plating of nickel onto irradiated parts of a TiO_2-adhered-alumina plate without resists was accomplished in an electroless nickel plating solution containing citric acid.

Such metals as Pt, Au, Pd, Ag, and Cu can be deposited onto TiO_2 particles with irradiation in solutions containing salts of these metal ions and sacrificial electron donors, such as alcohols or their oxidized products (aldehydes or acids). These phenomena have been widely known and have attracted much interest in terms of studies concerning the current doubling effect of the electron donors on semiconductor surfaces, the preparation of metallized semiconductor powders, or a new plating method.[1—4] However, few studies have been reported concerning the photoelectrochemical deposition of nickel (which has a negative reduction potential compared to the metals cited above) onto TiO_2 particles. We studied the possibility of the photoelectrochemical deposition of nickel onto TiO_2 particles using several kinds of TiO_2 and sacrificial reagents, and found that nickel deposits onto TiO_2 particles with irradiation under certain conditions. This paper reports on the depositon of nickel onto TiO_2 particles with irradiation and the formation nickel patterns on a TiO_2-adhered-alumina plate without resists.

Experimental

Materials and Experimental Apparatus. The TiO_2 particles used in the experiment were of the following two types:

TiO_2-1, which was purchased from Kojundo Chemical Co., Ltd. The crystal form is rutile, and its diameter is 1—2 μm.

TiO_2-2, which was purchased from Taki Chemical Co., Ltd. The crystal form is anatase. It is a sol-type TiO_2, and its diameter is ca. 80 Å.

The concentration of the TiO_2 particles was 10 $g\,dm^{-3}$. Nickel (II) chloride hexahydrate at a concentration of 0.1 M (1 M=1 $mol\,dm^{-3}$) was employed. Citric acid was employed as a sacrificial reagent; its concentration was 0.2 M. The pH value of the solution was adjusted to be between 3 and 11 by adding concd hydrochloric acid or sodium hydroxide aqueous solutions. A 250 W super-high-pressure mercury lamp (Ushio, USH250D) was employed as the light source. The light was applied through an IR-cutting filter to the solution in a test tube made of quartz. Using a water bath, the temperature of the solution was controlled to be ca. 60 °C. All of the experiments were carried out under the atmosphere.

Plating on an Alumina Plate. Degreased 96% alumina plates (Kyocera) were etched in a hydrofluoric acid aqueous solution of 2.5 M. The alumina plates were rinsed with ion-exchanged water, immersed in a TiO_2-2 solution of 10 $g\,dm^{-3}$, and dried at 85 °C. The amount of supported TiO_2-2 was ca. 3×10^{-5} $g\,cm^{-2}$. Some of the plates were heated at between 300 and 700 °C for 1 h before plating. An electroless nickel plating solution containing citric acid of 0.2 M, nickel (II) chloride hexahydrate of 0.1 M, and sodium phosphinate monohydrate of 0.1 M was employed for the plating. The pH value of the solution was 10. The temperature of the solution was ca. 60 °C. The plate was set in the electroless nickel plating solution about 1 mm behind a mask. Light was applied through the mask to the alumina plate for 30 s. After irradiation, the plate was kept in the electroless nickel plating solution for 3 h.

Measurement of Peel Adhesion Strength. Using a mask with 4 mm^2 (2 mm×2 mm) windows, nickel was plated onto the TiO_2-2 adhered alumina plate with irradiation in the electroless nickel plating solution. In order to compare this photo-initiated nickel pattern formation method with a conventional method, nickel layers with the same shape were electroless-plated onto the alumina plate with commercially available seeding solutions (Shipley, Cataprep 404, Cataposit 44, and accelerator 19) and a screen printing technique. These processes are shown in Fig. 1. The thickness of the plated nickel layers was ca. 3 μm in both cases. A copper wire of 0.8 mm in diameter was laid on the plated nickel layer and then soldered. One terminal of the copper wire was connected to a tensile tester, and the peel adhesion strength of the plated nickel layer was measured.

Results and Discussion

Deposition of Nickel. In the pH range from 6 to 10, the solutions containing both TiO_2-2 and citric acid turned to dark gray in color after irradiation for 1 h. In order to clarify this phenomenon, the solution was filtered and the residue on the filter paper was dissolved in concd nitric acid, hydrofluoric acid, and perchloric acid aqueous solutions. The Ni/Ti molar ratio of the residue was then analyzed by ICP-AES and expressed as a function of the irradiation time. The residue of the solution after irradiation for 16 h was also identified using an X-ray diffraction method. The results obtained with a solution of pH=6 are summarized in Fig. 2. In the case of TiO_2-1, the Ni/Ti molar ratio of the residue appeared to have a very low value. In the case of TiO_2-2, however, the Ni/Ti molar ratio of the residue became higher with the irradiation time and

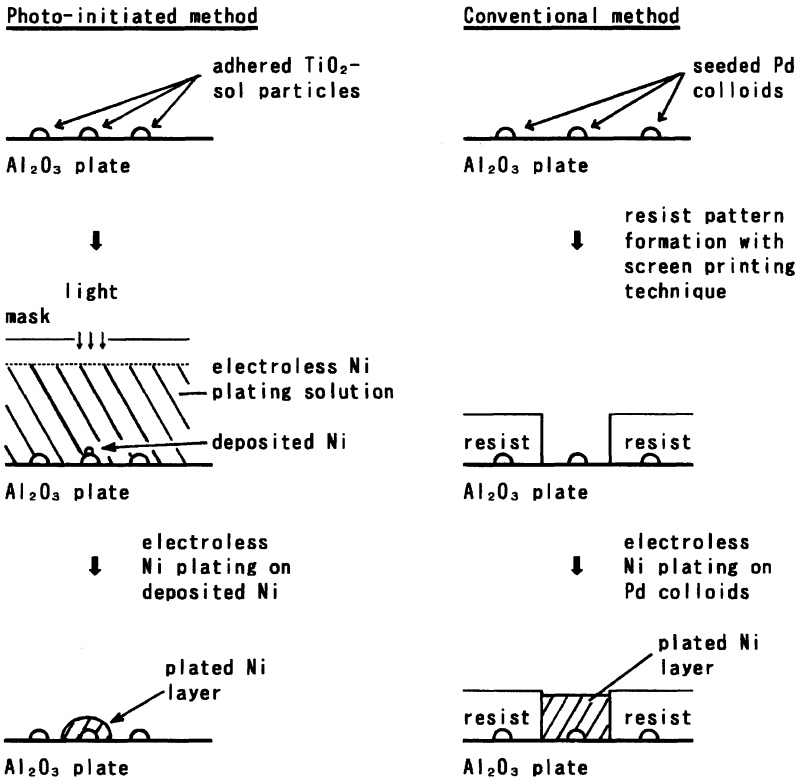

Fig. 1. Nickel-pattern plating by photo-initiated method and conventional method.

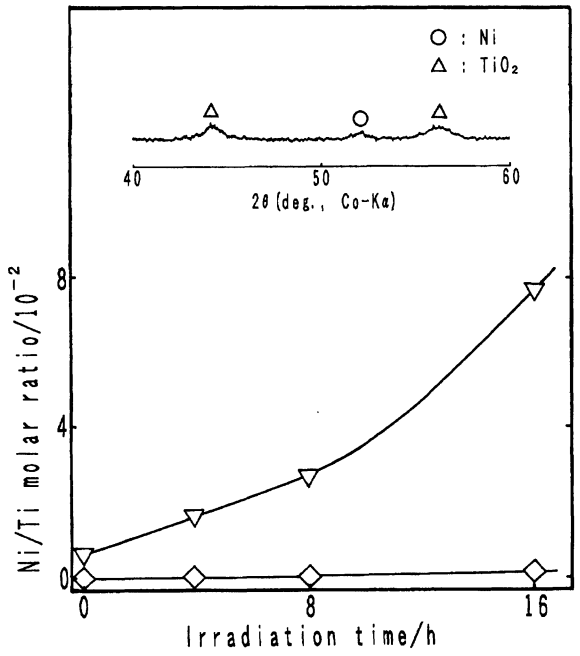

Fig. 2. Ni/Ti molar ratio of the residue vs. irradiation time: (◇) TiO_2-1 of 10 g dm^{-3} +citric acid of 0.2 M +$NiCl_2 \cdot 6H_2O$ of 0.1 M; (▽) TiO_2-2 of 10 g dm^{-3} +citric acid of 0.2 M +$NiCl_2 \cdot 6H_2O$ of 0.1 M. Inset: X-ray diffraction pattern of the residue.

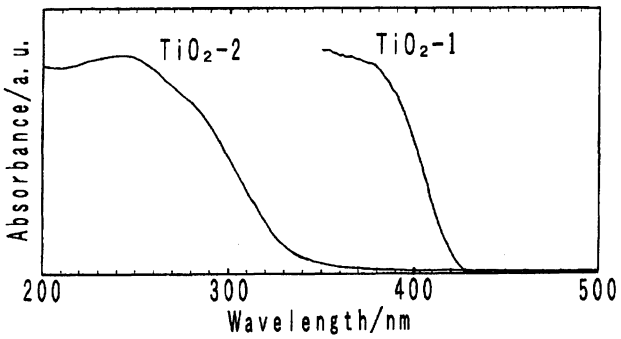

Fig. 3. Diffuse reflectance spectra of TiO_2 particles.

a small peak of the metallic nickel diffraction line was observed in the residue of a solution irradiated for 16 h. From these results, the change in the solutions containing both TiO_2-2 and citric acid with irradiation is thought to be caused by the deposition of nickel.

Figure 3 shows the diffuse reflectance spectra of TiO_2 particles employed in this study. The absorption edge of TiO_2-1 is about 420 nm, which corresponds to the band gap of the bulk crystal of the rutile previously reported.[5] On the other hand, the absorption edge of TiO_2-2 is about 330 nm, and its band gap is estimated to be 3.8 eV. This value is about 0.6 eV higher than the bulk crystal of the anatase previously reported.[5] Since the diameter of TiO_2-2 is ca. 80 Å, this blue-shift phenomenon of the diffuse reflectance spectrum is thought to be caused by the quantum size effect.[6]

The relationship between the flat band potential ($E_{f.p.}$/V vs. NHE) and the band gap ($E_{b.g.}$/eV) on oxide type semiconductors is well-known, as indicated

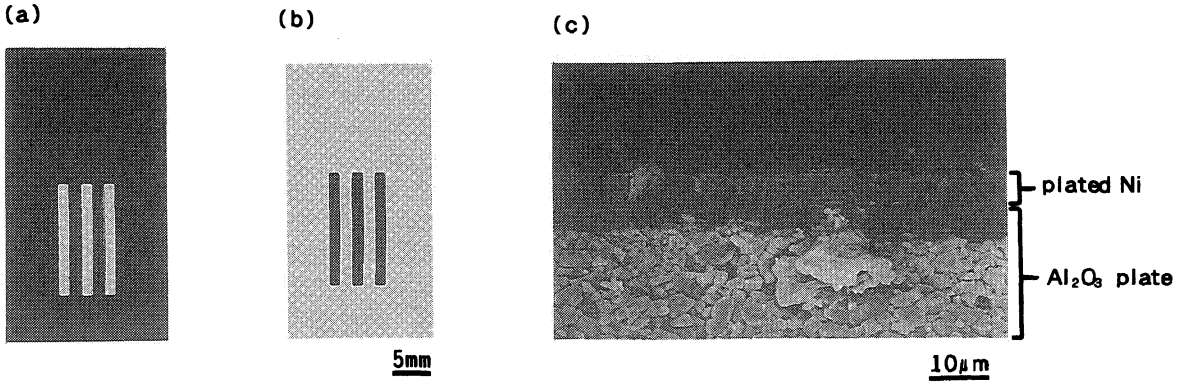

Fig. 5. (a) The mask. (b) Pattern of deposited nickel on the alumina plate. (c) SEM photograph of fractured nickel pattern.

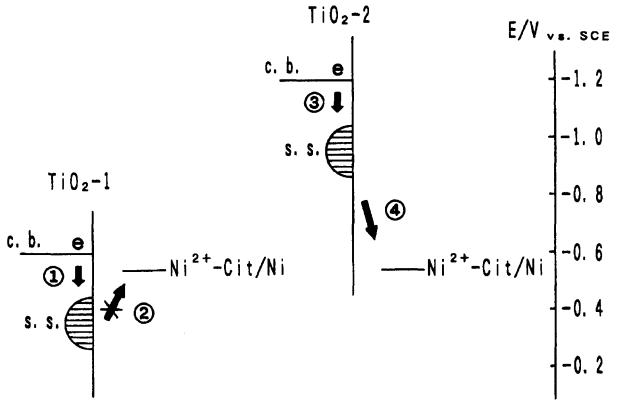

Fig. 4. Energy-level diagram for the photoelectrochemical deposition of nickel onto TiO_2 particles (pH=6).

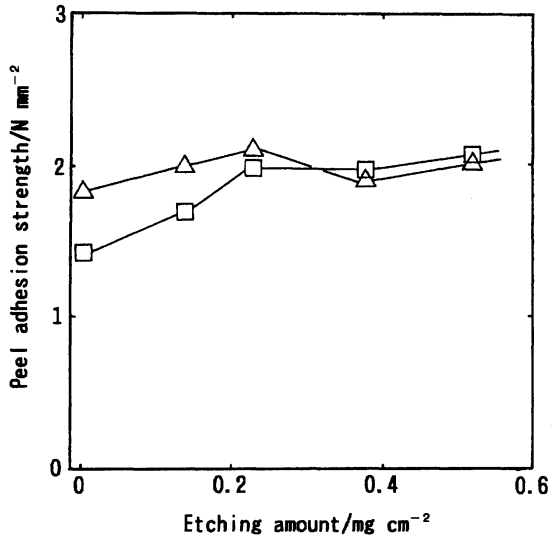

Fig. 6. Relationship between the peel adhesion strength of the nickel layer on the alumina plate and the etching amount of the alumina plate: (□) plated on a TiO_2-2-adhered-alumina plate without heat treatment before plating; (△) plated on an alumina plate activated with commercially available seeding solutions.

below:[7]

$$E_{f.p.} \fallingdotseq 3.0 - E_{b.g.}.$$

Since TiO_2 is an n-type semiconductor, the flat band potential is nearly equal to the potential of the conduction band (c.b.). Therefore, the potential of the conduction band of TiO_2-2 is estimated to shift by about 0.6 V towards the negative potential.

From these results, the deposition mechanism of nickel onto TiO_2-2 particles with irradiation is thought to be as shown in Fig. 4. TiO_2 particles absorb UV light and produce photoexcited electrons in the conduction band. The photoexcited electrons then flow to the surface states (s.s.) of the TiO_2 particles (①, ③). In the case of TiO_2-1, the photoexcited electrons in the surface states cannot flow to the Ni^{2+}-Cit complex (Cit=citric acid, ②). In the case of TiO_2-2, however, the photoexcited electrons in the surface states can flow to the Ni^{2+}-Cit complex (④) due to the potential shift of the conduction band towards the negative potential. Therefore, the nickel deposits onto the TiO_2-2 particles.

Formation of Nickel Patterns on an Alumina Plate. Citric acid is known to be a typical complexing agent for the Ni^{2+} ion in an electroless nickel plating solution. If the photoelectrochemical deposition of nickel occurs on a TiO_2-2-adhered-alumina plate in the electroless nickel plating solution, it is thought that the deposited nickel acts as a nucleus for the electroless nickel plating reaction and continuous plating of nickel occurs, even after irradiation. The results are shown in Fig. 5. The plating of nickel was observed on the irradiated parts of the TiO_2-2-adhered-alumina plate. As can be seen from the SEM photograph of the fractured nickel layer (Fig. 5 (c)), the thickness of the plated nickel layer was ca. 5 μm. These results indicate that the selective plating of nickel patterns on the alumina plate without resists was accomplished in the electroless nickel plating solution containing citric acid.

Peel Adhesion Strength of Plated Nickel. Figure 6 shows the relationship between the peel adhe-

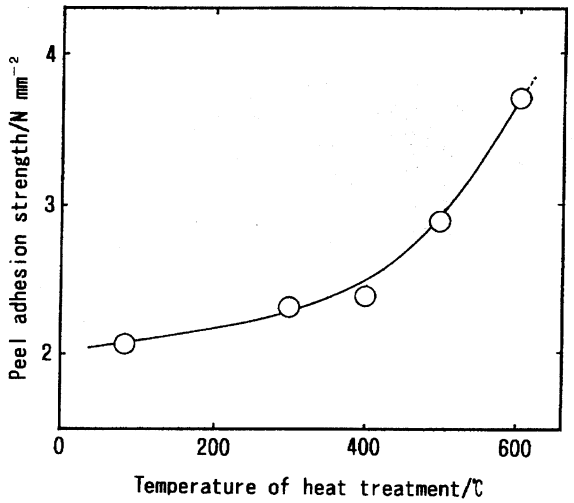

Fig. 7. Relationship betwen the peel adhesion strength of the nickel layer on an alumina plate and temperature of the heat treatment on an alumina plate before plating.

sion strength of the plated nickel layers and the etching amount of the alumina plate. In both cases, when the etching amount was below 0.2 mg cm^{-2}, the peel adhesion strength of the plated nickel layers became higher with the etching amount due to an anchoring effect. When the etching amount was more than 0.3 mg cm^{-2}, the peel adhesion strength of the plated nickel layers appeared to have a rather constant value. In this region, the peel adhesion strength of the nickel layers plated by the photo-initiated plating method was comparable to that plated by the conventional method.

Figure 7 shows the relationship between the peel adhesion strength of the plated nickel layers and the temperature of the heat treatment on the TiO_2-2-adhered-alumina plate. The etching amount of the alumina plate was ca. 5.2×10^{-1} mg cm^{-2}. The peel adhesion strength of the plated nickel layers became higher with the temperature of the heat treatment. Especially, when the TiO_2-2-adhered-alumina plate was heated at 600 °C for 1 h before plating, the peel adhesion strength became about twice as much as that for the plate treated by the conventional method. In this case, small flakes of the broken alumina plate sometiems adhered to the back of the plated nickel layers. This increase in the peel adhesion strength is thought to be caused by the sintering of TiO_2-2 particles to the alumina plate. When the temperature of the heat treatment was 700 °C, no deposition of nickel was observed. This phenomenon is thought to occur by either the cohesion of TiO_2-2 particles or the formation of a compound oxide between TiO_2 and Al_2O_3 of the alumina plate.

Compared to the conventional method shown in Fig. 1, the photo-initiated plating method has the following characteristics:

1. It does not require Pd colloids that act as nuclei for an electroless nickel plating reaction.
2. Nickel patterns are formed without resists.

It is very difficult to form resist patterns on a substrate that has steps or curved shapes at the surface. This method, therefore, is thought to be more effective for forming nickel patterns on the substrate than the conventional method if proper irradiation is performed on the substrate in the electroless nickel plating solution.

References

1) R. Baba, R. Konda, A. Fujishima, and K. Honda, *Chem. Lett.*, **1986**, 1307.
2) J. S. Curran, J. Domenech, N. Jaffrezic-Renault, and R. Philippe, *J. Phys. Chem.*, **89**, 957 (1985).
3) S. Sato, T. Kadowaki, and K. Yamaguchi, *Shokubai*, **26**, 360 (1984).
4) S. Morishita, *Chem. Lett.*, **1992**, 1979.
5) S. Okazaki, *Sikizai Kyokai Shi*, **60**, 333 (1987).
6) A. Nakamura, *Kogaku*, **19**, 10 (1990).
7) D. E. Scaife, *Sol. Energy*, **25**, 41 (1980).