Different Behavior in the Deposition of Platinum from HF Solutions on n- and p-Type (100) Si Substrates

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ABSTRACT

Platinum electroless deposition on silicon from HF solutions was studied by scanning electron microscopy and transmission electron microscopy, focusing the interest on the different evolution of the deposit on n- and p-doped samples. In both cases the final result was that a complete platinum layer was eventually formed, but the process was hindered on n^+ substrates which exhibited an induction period and displayed a more local behavior compared to p substrates. The results are discussed in terms of a global electrochemical process in which silicon is oxidized and platinum reduces injecting holes to the silicon valence band.

Introduction

Electroless metal deposition (EMD) processes are widely used in a variety of fields to provide metal coating of surfaces by simple immersion in a suitable aqueous solution. Many advantages of electroless coatings have been reported: deposition selectivity and purity, low operating temperature, planar topography, good filling characteristics, simplicity, and low cost of the process, which makes them very appropriate for industrial applications. Electroless coatings have been used for decorative plastic parts, printed circuit boards,[1] electrode preparation,[2] ohmic contacts on GaAs, [3] via hole filling, or ultralarge scale integration (ULSI) silicon metallization.[4,5]

EMD was introduced in 1946 by Brenner and Riddell[6] and has been widely studied. Its principles and behavior are well established[7] but many contributions, patents, and reviews are still published every year.[8] EMD is obtained by reduction of metal ions present in the solution by means of a chemical reducing agent. However, previous activation of the surface is often a key step, affecting the adhesion, resistivity, and selectivity of the deposited electroless coating. Activation is usually achieved by depositing small amounts of palladium on the surface from solutions containing HF and other acids.[9,10] Pd nuclei act as charge exchange and hydrogen evolution centers, thus initiating the electroless coating in the strict sense.

Solutions of ionic metals in HF have drawn interest recently either due to their activation role in EMD processes on semiconductors,[10-16] or to study the effect of metallic contaminants in wet cleaning processes for the microelectronics industry.[17,18] They have also been extensively used to reveal dislocations and lattice defects in silicon surfaces.[19]

Metal deposition from HF solutions is an electrochemical redox reaction in which both anodic and cathodic processes occur simultaneously at the Si surface while the charge may be exchanged through the substrate. Fluoride ions in acid solutions serve not only to prevent the formation of silicon oxide but also to solubilize the silicon material as SiF_6^{2-} complexes. The global chemical reaction of the redox couple is

$$M^{n+}(aq) + Si^0(s) + 6F^-(aq) = M^0(s) + SiF_6^{2-}(aq)$$

which can be separated into two half-cell processes

$$M^{n+} + ne^- = M^0 \qquad E^0(M^{n+}/M^0)$$

$$SiF_6^{2-} + 4e^- = Si^0 + 6F^- \qquad E^0(Si^{4+}/Si^0) = -1.20\ V$$

always considering the total reduction of metal ions. Of course, this global chemical reaction does not give information about the detailed mechanism of the deposition process, and the electrons in the half-cell equations can have different thermodynamic potential because the electron transfer could be through a different interphase, *i.e.*, platinum solution or silicon solution interfaces. Thus, the metallic ions reduce and deposit on the surface forming nuclei while the silicon substrate is oxidized and etched away helped by the presence of fluoride, resulting in an increase of silicon surface roughness and pitting.

In the case of platinum deposition, the electrochemical reaction produces highly pure, polycrystalline nuclei and in the first stages of the process it seems plausible to understand that a direct chemical reaction between platinum ions and silicon atoms takes place. X-ray photoelectron spectroscopy (XPS) measurements on similarly prepared samples demonstrated the spontaneous room temperature silicidation of the deposits.[20] The effect of pH has also been studied[21]: an increase of solution pH from the currently used value 1.5 to a value of 3 promotes Si etching and as a consequence the metal nuclei get nailed into the etched substrate. The ratio between metallic platinum and platinum silicide now increases as deduced from XPS measurements.

Silicon oxidation or metal reduction is initiated at defects on the surface such as scratches or contamination sites[12] or kinks, steps, and areas where ions are able to react because they are more chemically active than the H-terminated areas.[18] Of course, the EMD rate depends on the defect concentration of the substrate, as we have demonstrated by the increase in EMD coverage on silicon samples previously bombarded with different Ar ion doses. Crystal and surface defects in Si are decorated in this way by using EMD-like solutions.[19]

It seems evident that since the electrical charge is transferred through the substrate the electric properties of silicon will play a role on the deposition mechanism which may be different for differently doped samples. In the present contribution, we have studied the platinum deposition on (100) silicon as obtained from platinum fluorinated solutions, and we have focused our effort on the role of silicon doping. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the morphology of the advanced stages of deposition, supplying new and complementary information to the results on first stages published elsewhere.[16,20]

Experimental

All solutions were prepared with p.a. grade reagents and triply distilled water (18 MΩ resistivity), which was also used for all water rinses. Etching solutions were freshly prepared from 40% HF "Suprapur" grade supplied by Merck and low conductivity water. The substrates used in this study were 2 in. diam CZ (100) silicon wafers supplied by Crysteco Company in isolated boxes with quality control signature. p-Type samples were of two doping levels, one having a resistivity ranging between 12.0 and 18.5 Ω cm and the other between 0.8 and 1.25 Ω cm. n-Type samples have a resistivity ranging between 0.01 and 0.02 Ω cm. Previous to each deposition experiment the native oxide layer was etched in an aqueous HF solution (the 40% HF

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solution was diluted ten times, the final pH of the solution being less than 2) for a few seconds, until the sample showed a hydrophobic behavior.

Plating solutions were obtained by dissolving small amounts of a metal salt in the aqueous HF etching solution. Sodium or potassium hexachloroplatinate(IV) powder, $Na_2PtCl_6 \cdot 6H_2O$ or $K_2PtCl_6 \cdot 6H_2O$ (Johnson Matthey GmbH) were used to yield a final platinum concentration in solution of 1.0 m*M*. Immediately after removal of the protective oxide layer, samples were immersed in the solution, which was stirred, and held vertically during deposition. Typical deposition times ranged between 1 and 60 min. All depositions were carried out under controlled ambient conditions at room temperature. Experiments under illumination were done using a 35 W tungsten halogen lamp.[22]

Morphological characterization of the deposited samples was carried out by SEM either in LEO Stereoscan 360 or a Cambridge S-120 equipped with a PCXA Link electron dispersive x-ray analysis (EDX). TEM experiments were performed in a Philips CM30 (300 keV) TEM equipped with a Q2300 Link EDX.

Results and Discussion

In order to achieve a uniform and reproducible layer the solution was stirred during deposition, producing a laminar flow perpendicular to the silicon surface. Stirring guarantees both dissolution of the oxidized silicon as fluorine compounds and continuous supply of platinum ions to the surface. In the absence of convection, the process is diffusion controlled[15] and nuclei deposit in surface defects, tending to grow rather than let new nuclei appear, thereby creating a defect revealing behavior.[19]

For all types of substrate, the samples were evenly covered by a platinum thin film after a 60 min deposition. SEM images show a grain structure and the coalescent grains have sizes below 1 μm. Sometimes the continuity of the layer is broken by nondeposited chinks, producing a cracked appearance. Figure 1 shows a SEM micrograph of a p-Si sample deposited for 60 min. The surface coverage is homogeneous and coalescence has been achieved. Figure 2 shows an intentionally produced scratch on the same p-Si substrate after only 15 min deposition showing that deposition starts and develops much earlier if the surface has defects such as scratches. Magnification is the same as Fig. 1.

Although the final platinum film appears very similar for p- and n-doped substrates, deposition proceeds very differently on them. In order to demonstrate the different behavior, Fig. 3 shows SEM micrographs of p^+ (a, b, c) and n^+ (d, e, f) silicon substrates after deposition for 15 (a, d), 30 (b, e), and 60 min (c, f). Silicon p- substrates were also examined and showed no remarkable differences with p^+. For the p^+ samples, a progressive nucleation process is observed in which platinum nucleates and grows on the surface until a thin layer is formed. Previous atomic force microscopy (AFM) work on the first stages of deposition[16,20] demonstrated that the bare silicon surface is simultaneously etched producing an overall increase in surface roughness that cannot be observed by SEM. The surface etching is particularly evident in the surroundings of the nuclei, and it is not attributable to the presence of HF alone, since it only develops when metal ions are added to the HF solution. Correspondingly, the deposition is not possible from an aqueous solution of the metal ions in the absence of HF. On the n^+ samples, a coalescent layer of metallic platinum takes longer to develop. In fact, after 30 min of deposition the surface presents numerous deep pits but only a few platinum nuclei, with sizes below 100 nm. For the same deposition time, the p^+ sample is mostly covered by platinum. The nuclei on the n^+ silicon have often deposited surrounding a deep etching pit. In fact, this feature taking part in n^+ substrates is straightforward related to the occurrence of fuzzy white areas in the SEM images as shown in Fig. 3e. Their frequency is lower than that of the previously mentioned nuclei but with sizes of some hundreds of nanometers. We discuss this subject below.

Enhanced silicon etching and platinum deposition occur from the very beginning in p^+ samples in a continuous process. The deposited platinum forms nuclei which act as local cathodes. These nuclei eventually coalesce, reducing the exposed area of silicon substrate and forming a grain structure. Then only the silicon intergrain boundaries act as local anodes from which the oxidized silicon is continuously extracted. In the first elementary process to develop a nuclei, oxidation of a silicon atom implies the capture of holes by an intrinsic surface state.[23] In every part of a free surface in a p-type substrate, this process should be easier due to the availability of holes. Holes are directly injected from the solution into the silicon by platinum ions reducing on the surface[24] and keeping charge neutrality. On the other hand, in n^+ samples, etching and deposition are still hindered to some extent[20] due to the lack of holes in the substrate. Now, the preferential sites for the etching and deposition are the surface flaws. After formation of some nuclei, silicon oxidation becomes facilitated taking into account the enhanced conditions for hole injection around the formed Pt/Si contact zone. Therefore, platinum deposition takes place filling the originated pits along the revealed defects. In these first stages the platinum deposition displays a more local behavior than that found in the p-type substrate. Finally, as the distribution of these pits increases, the deposition ends in a more uniform way, resulting in a coalescent thin film similar to that formed in p^+ doped silicon. This standpoint is further supported by the fact that the local behavior is enhanced in the absence of light (*i.e.*, photogenerated holes), as shown by some preliminary experiments. The p-type substrate is slightly affected by a change in the illumination, but n^+ substrates

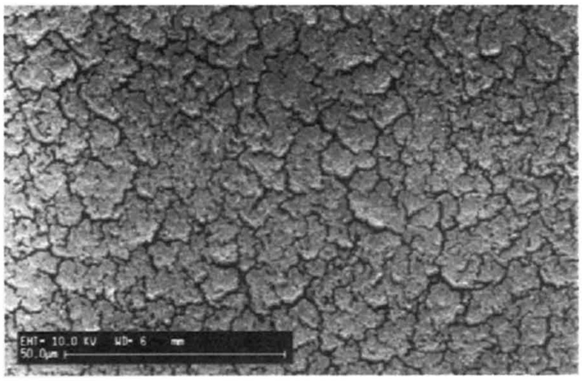

Fig. 1. SEM micrograph of a platinum deposit on a silicon p substrate after immersing the sample in the plating solution during 60 min.

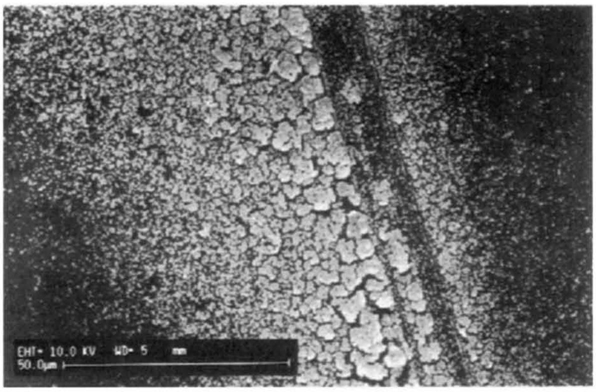

Fig. 2. Deposition is preferential on surface flaws: coalescence is achieved in only 15 min on an intentionally produced scratch on p-Si. Magnification is the same as Fig. 1.

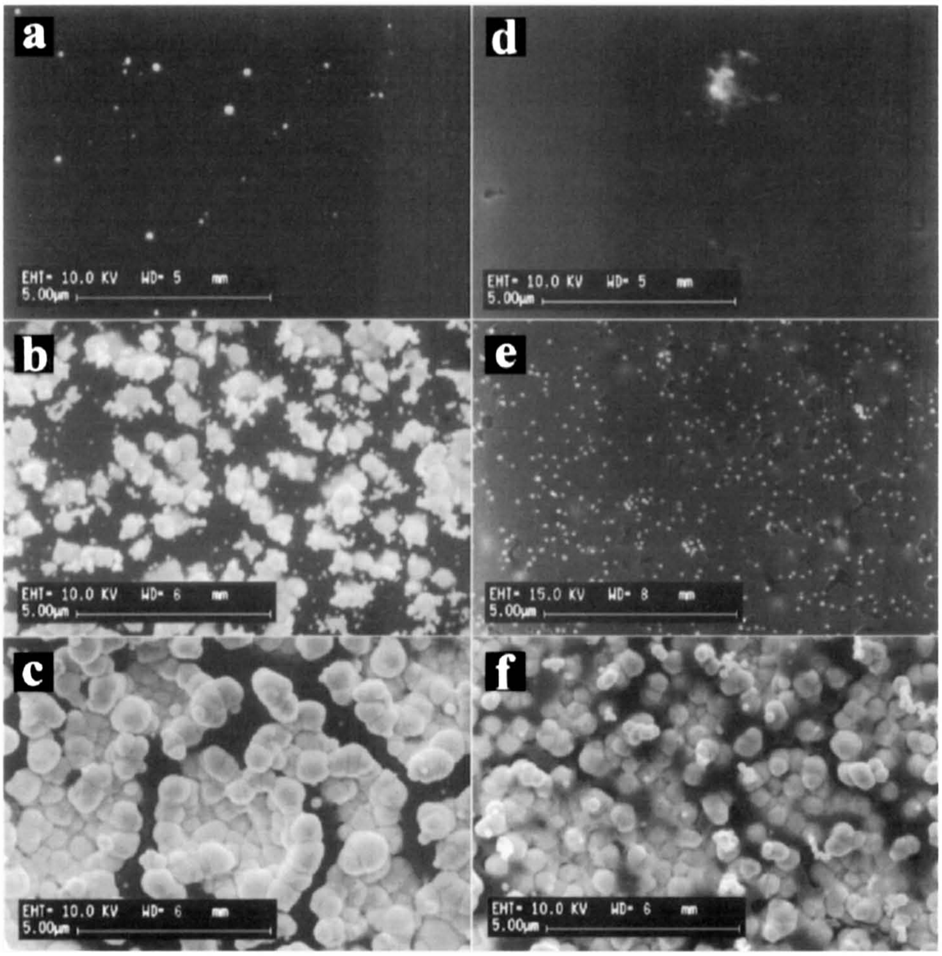

Fig. 3. Series of SEM micrographs showing the evolution of the electroless platinum deposit on p$^+$ (a, b, c) and n$^+$ (d, e, f) silicon substrates. Magnification is the same for all images. Deposition times are 15 (a, d), 30 (b, e), and 60 min (c, e). In (e), the fuzzy white areas referred in the text are observed.

suffer a big change: in the dark, only small nuclei are formed around the corresponding etchpit and the rest of the silicon surface remains unaltered. With the clean room lights turned on, nucleation is evident and homogeneously distributed. Illumination with the tungsten lamp produces an increase of a factor of ten in the nucleation demonstrating the expected sensitivity of n-type substrate to dispose electrons to the conduction band.

This particular behavior is demonstrated by the presence of fuzzy white areas in the SEM image of an n$^+$ sample (Fig. 3e). These areas can be resolved by varying the SEM electron-beam accelerating voltage. Image formation in SEM has contributions arising from both secondary and

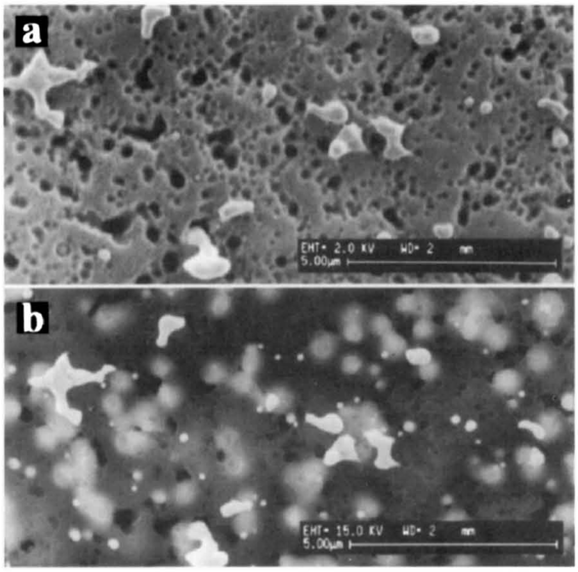

Fig. 4. SEM micrographs of the same region showing the effect of backscattered electrons in the SEM image formation. The sample is a n$^+$ silicon substrate where platinum has been deposited for 30 min. The average BS electrons information depth is only 14 nm at 2 keV (a) but reaches 431 nm at 15 keV (b), clearly showing the underneath platinum nuclei (see text for details).

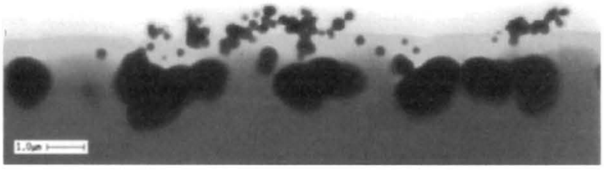

Fig. 5. Cross-sectional TEM micrograph of a n$^+$ sample deposited for 30 min as that of Fig. 4. The nuclei distribution suggested by Fig. 4b is now clearly visible.

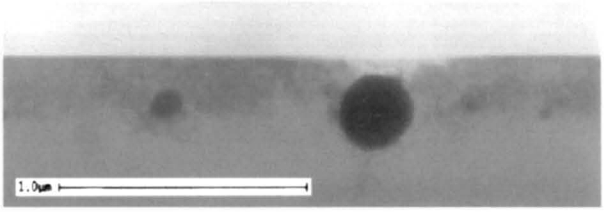

Fig. 6. Cross-sectional TEM micrograph of a n$^+$ sample deposited for 10 min. A few platinum nuclei have been deposited and the topmost silicon layer exposed to the EMD solution has a different contrast than the bulk.

backscattered (BS) electrons. The BS electrons are greatly affected by the accelerating voltage: a standard Monte Carlo simulation of the backscattering process using a 2 keV electron-beam on a silicon sample produces an average BS electrons information depth of 14 nm and the maximum depth reached by any electron is 37 nm. In the case of a 15 keV electron-beam, the corresponding values are 431 nm and 1.1 μm, respectively. Thus, the SEM image taken with a 2 keV beam and depicted in Fig. 4a shows only some nuclei deposited on a strongly etched substrate. The same region imaged at 15 keV reveals the existence of nuclei beneath the surface level (Fig. 4b). In order to corroborate the position of these nuclei, a cross section of the same sample was imaged by TEM clearly showing the distribution (Fig. 5) of the nuclei underneath the silicon surface.

These nuclei are not just nailed or inlaid within the substrate as a result of the enhanced silicon etching as we reported previously in the case of p-type samples. Instead, the nuclei seem to have grown under the surface, possibly as a consequence of the electrical potential reached at the bottom of pits during corrosion. It is well known that electrical potential can drop several hundred of millivolts between the sample surface and the bottom of a pit during pitting corrosion of metallic electrodes, and in the case of the electrochemical etching of metals that current lines converge into the surface pits.[25] Figure 5 taken after 30 min of platinum deposition and shows a high density of nuclei within a layer of approximately 1 μm thick. To better understand that platinum nuclei grow inside the pit, a cross section of a sample deposited only for 10 min was also imaged by TEM and the result is presented in Fig. 6. Now, the density of nuclei underneath the surface is low and the surface roughness is mainly the value at the bare silicon sample. Platinum nuclei are already under the surface and a modified darker region can be observed at the topmost Si layer. This thin layer has a porous morphology and appears in the entire Si surface exposed to the working solution most likely as a result of the anodization process. Work is in progress to characterize this porous layer and also to complete the acknowledgment of the mechanisms involved in the platinum deposition on p- and n-doped samples.

Conclusions

A platinum thin film has been deposited on silicon from HF solutions by electrochemical displacement deposition. In both n- and p-type silicon substrates, deposition of platinum nuclei is accompanied by etching of the silicon surface, and the whole chemical reaction can be interpreted when the stationary state is reached in terms of a redox couple (platinum reduction and deposition/silicon oxidation and dissolution) that exchanges charge through the substrate. However, depending on the type of substrate, the conditions for the holes injection step have been found to be different. So, the type and level of doping of the silicon substrates greatly affects the evolution of the process. In comparison with p^+ samples, deposition is initially hindered on n^+ substrates giving rise to an induction period. In n^+ sample deposition and subsequent etching deposition occurs more locally, the nuclei grow in the bottom of formed pits and grow around the pits on the surface, finally forming a metallic platinum thin film. The lack of holes in the n^+ substrates seems to be the cause, since the only sources for holes in the substrate are the injection from metal ions in the solution or holes photogenerated in the silicon bulk. In the case of p substrate, nucleation develops on the surface, and the rate of the process seems to be controlled by the etching of silicon.

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REFERENCES

1. R. M. Kennedy, K. Minten, X. Yang, and D. F. Evans, *J. Vac. Sci. Technol.*, **B9**, 735 (1991).
2. M. M. Murphy, J. van Herle, A. J. McEvory, and K. Ravindranathan Thampi, *This Journal*, **141**, L94 (1994).
3. L. A. D'Asaro, S. Nakahara, and I. Okinaka, *ibid.*, **127**, 1935 (1980).
4. C. H. Ting and M. Paunovic, *ibid.*, **136**, 456 (1989).
5. Y. S. Shacham-Diamand, V. Dubin, and M. Angyal, *Thin Solid Films*, **266**, 93 (1995).
6. A. Brenner and G. E. Riddell, *J. Res. Natl. Bur. Stan.*, **37**, 31 (1946).
7. See, for example, *Modern Electroplating*, F. A. Lowenheim, Editor, John Wiley & Sons, Inc., New York (1974).
8. See, for example, M. Paunovic, T. Nguyen, R. Mukherjee, C. Sambucetti, and L. T. Romankiw, *This Journal*, **142**, 1495 (1995); C. Y. Mak, *MRS Bulletin*, **XIX** (8), 55 (1994).
9. See, for example, A. F. Arnold, U.S. Pat. 3,857,733 (1974) of the recipes in Ref. 2 and 3.
10. C. Longo, P. T. A. Sumodjo, and F. Sanz, *This Journal*, **144**, 1659 (1997).
11. G. Stremsdoerfer, H. Perrot, J. R. Martin, and P. Cléchet, *ibid.*, **135**, 2881 (1988).
12. L. A. Nagahara, T. Ohmori, K. Hashimoto, and A. Fujishima, *J. Electroanal. Chem.*, **333**, 363 (1992).
13. L. A. Nagahara, T. Ohmori, K. Hashimoto, and A. Fujishima, *J. Vac. Sci. Technol.*, **A11**, 763 (1963).
14. K. K. Yoneshige, H. G. Parks, S. Raghavan, J. B. Hiskey, and P. J. Resnick, *This Journal*, **142**, 671 (1995).
15. O. M. R. Chyan, J. J. Chen, H. Y. Chien, J. Sees, and L. Hall, *ibid.*, **143**, 92 (1996).
16. P. Gorostiza, J. Servat, J. R. Morante, and F. Sanz, *Thin Solid Films*, **275**, 12 (1996).
17. T. Ohmi, T. Imaoka, I. Sugiyama, and T. Kezuka, *This Journal*, **139**, 3317 (1992).
18. H. Morinaga, M. Suyama, and T. Ohmi, *ibid.*, **141**, 2834 (1994).
19. P. Gorostiza, J. Servat, F. Sanz, and J. R. Morante, in *Defect Recognition and Image Processing in Semiconductors*, A. R. Mickelson, Editor, p. 293, Institute of Physics Publishing Ltd., Bristol, England (1996), and the references therein.
20. P. Gorostiza, R. Díaz, J. Servat, F. Sanz, and J. R. Morante, *This Journal*, **144**, 909 (1997).
21. P. Gorostiza, J. Servat, J. R. Morante, and F. Sanz, in *Silicide Thin Films Fabrication, Properties and Applications*, R. Tung, K. Maex. P. W. Pellegrini, and L. H. Allen, Editors, Vol. 402, p. 611, MRS Publications, Pittsburgh, PA (1996).
22. I. Teerlinck, H. F. Schmidt, A. L. P. Rotondaro, T. Q. Hurd, L. Mouche, P. W. Merlens, M. Meuris, and M. M. Heyns, Abstract 470, p. 745, The Electrochemical Society Extended Abstracts, Vol. 95-2, Chicago, IL, Oct. 8-13, 1995.
23. S. R. Morrison, *Electrochemisty at Semiconductor and Oxidized Metal Electrodes*, p. 283, Plenum Press, New York (1980).
24. P. Allongue, in *Advances in Electrochemical Science and Engineering*, Vol. 4, H. Gerischer and C. W. Tobias, Editors, p. 42, VCH Verlagsgesellschaft GmbH, Weinheim (1995).
25. D. Pletcher and F. C. Walsh, in *Industrial Electrochemistry*, 2nd ed., Chapman and Halland, University Press, Cambridge (1980).