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Effects of Nickel and Palladium Activations on the Adhesion and I-V Characteristics of As-Plated Electroless Nickel Deposits on Polished Crystalline Silicon

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We present a study of the adhesion and current-voltage characteristics of as-plated electroless nickel deposits on polished crystalline silicon activated using nickel and palladium. A highlight of this study is the derivation of practically significant trends by collating the results of a large number of simple experiments as a function of substrate doping polarity, doping level, plating area, and plating duration. The study reveals that palladium activation is most effective on P^+ substrates while nickel activation is most effective on N^+ substrates, due to the requirement of substrate holes in the former activation and electrons in the latter. An activation process always improves adhesion, but, in some cases, degrades the electrical properties of the plating-silicon interface, because it introduces an intermediate silicide layer between nickel and silicon. Electroless nickel layer adheres better to nickel activated silicon, than to palladium activated silicon. However, the rectifying nature of the electroless nickel contacts on palladium activated silicon is superior to those on nickel activated silicon. Further, palladium silicide forms at 200°C, which is much lower than the temperature of 400°C required for nickel silicide formation.

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Since its proposal four decades ago,¹ electroless nickel plating has found increasing application in the silicon industry, for contact metallization,^{2,3} via-hole filling of integrated circuits (ICs) to interconnect the different metallization layers,⁴ and fabrication of metal microstructures in microelectromechanical systems (MEMS).⁵ Electroless nickel plating is an autocatalytic reaction, which requires a catalytic substrate for nucleation and growth. Amorphous, porous, or heavily etched silicon substrates are sufficiently catalytic for this purpose,^{6,7} but not polished crystalline silicon substrates, whose catalytic nature also depends upon substrate doping. Insufficiently catalytic surfaces either do not plate, or give poor plating adherence. To make them catalytic, an activation step is usually introduced prior to electroless plating.

We report a comprehensive study of the adhesion and currentvoltage characteristics of as-plated electroless nickel deposits on polished crystalline silicon activated using nickel and palladium. The characteristics have been measured for different doping levels, and, in addition, adhesion has been measured as a function of area and plating duration. This study reveals several interesting trends not reported in literature,^{1-5,8} and should be useful, because polished (on at least one side) and crystalline form of silicon substrates are the most widely used in the semiconductor industry.

Substrate Preparation

Polished substrates with a mirror finish and $\langle 111 \rangle$ orientation were employed, which were cut into areas of 0.5 \times 1 cm, 1 \times 1 cm, and 1×2 cm. The lightly doped substrates had a resistivity of 0.5-1 Ω cm, which amounts to a doping level of 4-8 \times $10^{15}/\text{cm}^3$ for phosphorus doped (N-type) substrates and $1-2 \times 10^{16}/\text{cm}^3$ for boron-doped (P-type) substrates. Heavily doped surfaces were obtained by diffusing boron and phosphorus into lightly doped substrates of opposite polarity. The sheet resistivity and junction depth were measured to be 17.4 Ω/\Box and 1.8 μ m for boron, and 3.9 Ω/\Box and 5.15 μm for phosphorus. These amount to P^+ and N^+ surfaces with doping of $\sim 10^{20}$ /cm³ estimated from Irvin curves which show surface doping as a function of the sheet $\rho \times$ junction depth product. Care was taken to remove the glass formed during boron diffusion. An oxide layer of thickness $>0.3 \mu m$ was grown on all substrates (on heavily doped substrates this was done during drive-in of the diffusion).

On the substrates meant for adhesion measurements, the oxide layer on the polished surface of the substrate was etched away, while protecting the opposite (rough) surface using a photoresist. The substrates meant for I-V measurements were patterned to create 0.5×0.5 mm windows into the oxide layer of the polished surface, for metal contact. During this process, the oxide on the rough surface of the substrate was removed.

Because electroless plating is known to be very sensitive to surface conditions, the surface resistivity or surface doping is more relevant than the bulk or sheet resistivity, and also, substrate needs thorough cleaning. The substrate was cleaned as follows. It was immersed, under mild agitation, in trichloroethylene, which was heated to the boiling point, to remove the organic impurities. To remove the remnants of trichloroethylene, the substrate was immersed in hot acetone under agitation. It was then rinsed in deionized (DI) water, and boiled in nitric acid to remove metallic impurities. After another rinse in DI water, it was subjected to one of the surface treatments, palladium activation and nickel activation, for the purpose of improving its catalytic nature. These treatments are discussed below.

Activation

Palladium activation was achieved using a solution of PdCl₂ and NH₄F in dilute HF, prepared as follows.⁹ A palladium chloride stock solution was prepared by dissolving 0.05 gm of palladium chloride in 1.5 mL of HCl and 10.5 mL of DI water. An NH₄F stock solution is prepared by dissolving 11.2 gm of NH₄F in 88 mL of DI water. Before activation, 0.8 mL of palladium chloride stock solution and 16 mL NH₄F stock solution were mixed with 7.3 mL of 10% HF solution and 48 mL of DI water. Thorough mixing was ensured by vigorous agitation and allowing a settling time of 15 min. 5 mL of this activator solution was used for activating each substrate. The substrate was dipped in 10% HF for 5 s to remove any native oxide, and immersed in the activator solution for 2 min under agitation, at room temperature. Then, it was thoroughly cleaned in DI water, dried, and annealed in nitrogen ambient at 200°C for 30 min to convert the deposited palladium into palladium silicide. On removal from the furnace, the substrate was swabbed gently with wet cotton to remove any nonadherent palladium deposit, and thoroughly rinsed in DI water. The entire process consisting of dilute HF dip, immersion in palladium activator solution, annealing, and swabbing, and DI water rinse was repeated, to improve adhesion.

The nickel activation process was similar to the palladium activation described above. After a 5 s 10% HF dip, the substrate was immersed for 2 min in an alkaline electroless nickel bath having the composition: nickel chloride, NiCl₂·6H₂O (30 g/L), sodium hypophosphite, Na₂H₂PO₂ (10 g/L), sodium citrate,

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Figure 1. Measurement setups for (a) adhesion and (b) current-voltage characteristics.

 $Na_3C_6H_5O_7 \cdot 2H_2O$ (84 g/L), and ammonium chloride, NH_4Cl (50 g/L). A bath pH of 8-10 and temperature of 90-95°C was maintained during immersion. For each substrate, 20 mL of the solution was used. Note that, a larger volume of solution than in the palladium activation described above is used, due to elevated temperature of the process, during which the pH change may be significant due to the loss of ammonia, if smaller volume of the solution is used. On removal from the solution, the substrate was annealed in nitrogen ambient for 30 min to convert the deposited nickel into nickel silicide; an annealing temperature of $400^{\circ}C$ was employed, because $200^{\circ}C$ was found to be inadequate for improving adhesion. The annealed substrate was boiled in nitric acid for 5 min to remove any nonadherent remnants and rinsed thoroughly in DI water.

Electroless Nickel Plating

The activated substrate was immersed in 20 mL of the alkaline electroless nickel bath described above, for 2 min. The plated substrate was rinsed thoroughly in DI water and dried with air gun. This process gave a plating thickness of \sim 0.2 µm measured as follows. The plating was done over a window opened into a wet oxidized wafer having a known (measured) oxide thickness of 0.3 µm, and the difference between the thickness of the plating and the oxide was obtained using a surface profiler. The plating thickness is a function of bath composition, temperature, pH, and plating duration, which were controlled by taking a fresh solution for every experiment. The thickness depends on surface conditions also. The conclusions of our study are not affected by this fact.

Adhesion and Current-Voltage Measurement Procedure

Adhesion strength was measured by a pull test (see Fig. 1a). The substrate was sandwiched between two metal blocks using extremely strong, rapid cure cyanoacrylate adhesive (ANABOND 202, Anabond Pvt. Ltd., Chennai, India). Prior to this, the metal blocks were cleaned in acetone and isopropyl alcohol, and heated in an oven along with the substrates at 120°C for 15 min to remove adsorbed moisture in the metal block. The blocks were pulled apart @ 1 mm/min using a universal testing machine (UTM, model-INSTRON, no. 4301) until they separated. The force required for separation was measured.

The plated substrates used in current-voltage measurements were heated in nitrogen ambient at 150°C for 5 min, prior to measurement, to remove any moisture, which is a cause of instability in characteristics. The measurement set up is shown in Fig. 1b, along with a cross-section of the substrate and an equivalent circuit giving the elements-R_B, R_C, and R_S, which contribute to the measured characteristics of the electroless nickel—polished silicon contact. The back contact resistance R_B is much less than the contact resistance, R_C, of the nickel-silicon contact, on account of the surface roughness and much larger area associated with the former. For the substrate doping and geometry described above, the substrate resis-



Figure 2. Adhesion as a function of area for different surface doping. (a) No activation, (b) palladium activation, and (c) nickel activation. The numbers indicate the substrate area in cm^2 .

tance R_S was estimated to be several times less than the measured resistance.¹⁰ So, the measured characteristics reflect the properties of the plated metal-silicon contact.

Measured Results

First, we present the measured adhesion trends in Fig. 2 and 3. The end points of a vertical segment in each of these figures indicates the two adhesion values obtained during two separate but identical experiments; the length of the segment represents the dispersion arising out of factors beyond experimental control. The doping level of substrates in Fig. 3 corresponds to those used in MEMS applications, where thick plating may be necessary. The figures show that activated substrates provide higher adhesion than unactivated ones. The other trends are discussed below.

For palladium activation, the improvement in adhesion strength is maximum in the case of heavily doped P-type substrate, and decreases progressively as the substrate becomes less P-type or more N-type. Interestingly, on P-type substrates, whether lightly or heavily doped, adhesion strength decreases with substrate area;



Figure 3. Adhesion as a function of plating duration for lightly doped Nand P-type substrates (a) No activation, (b) palladium activation, and (c) nickel activation. The numbers indicate the plating duration in minutes; plating area = 1 cm^2 .

however, on N-type substrates, no particular trend is observed in this regard. Adhesion decreases as the plating duration increases.

For nickel activation, the results are shown in terms of absolute values of adhesion, unlike in the case of palladium activation, where the adhesion is reported per unit area. This is because, for nickel activation, during pull-test associated with adhesion measurement, the failure occurred in silicon rather than at the nickel-silicon interface, where the failure occurred for palladium activation. Hence, the reading shown on the adhesion axis corresponds to the fracture in silicon rather than to the nickel-silicon adhesion, which is higher than the reading shown. Thus, the trends in adhesion of nickel to silicon as a function of doping, area and duration become irrelevant, and what is significant is that nickel activation provides a much higher adhesion than palladium activation, independent of doping, area and duration.

Next, we present the current-voltage characteristics in Fig. 4. The characteristics were fairly uniform over the substrate area. The characteristics are seen to be Schottky type for lightly doped substrates



Figure 4. Current-voltage characteristics as a function of the surface doping. Pd-palladium activation, Ni-nickel activation, and None-no activation.

and ohmic for heavily doped substrates. The forward voltage for 1 mA current extracted from this data is shown in Fig. 5. The forward voltage for nickel activation is higher than that for palladium activation, for lightly doped N or P-type and P⁺ substrates, even though nickel activation provides better adhesion than palladium activation for these substrates. Similarly, on N⁺ substrates, the forward voltage without any activation is lower than that with either nickel or palladium activation, which provide as good or better adhesion. These facts show that the means of improving mechanical properties of the nickel-silicon contact system do not always improve electrical prop-

	No activation	Palladium activation	Nickel activation
N+	0.03	0.11	0.05
N	0.45	0.45	0.6
Ρ	0.45	0.35	1.1
P⁺	0.08	0.02	0.04



Figure 5. Forward voltage at 1 mA current for contacts on unactivated and activated substrates.



Figure 6. Model of the electroless nickel-polished silicon interface. (a) Top view showing nucleation sites, (b) cross-section showing unactivated and activated silicon. The diagram is not to scale (nickel thickness \leq silicon thickness).

erties, and that activation, which always improves adhesion, does not necessarily reduce contact resistance. The significant increase in forward voltage on N⁺ substrates due to palladium activation points out the disadvantage of using this activation on N⁺ substrates. On the other hand, the low adhesion and high forward voltage, observed for P⁺ substrates without nickel or palladium activation, establish the necessity of activation for these substrates.

Discussion

The observed variation in the effectiveness of the activation processes as a function of doping level reveals the polarity of charge carriers required for the electrochemical reactions associated with these processes. The trends in this variation are different for nickel and palladium activations, indicating that the charges required in these are of opposite polarity. The increasing effectiveness of palladium activation in improving adhesion and lowering forwardvoltage on substrates with higher hole concentration reveals the requirement of positive charges in palladium deposition. For nickel activation, what could not be revealed in adhesion tests due to the plating adhesion being higher than silicon fracture strength is brought out in current-voltage measurements. The fact that the forward voltage on N⁺ substrates is lower when these are unactivated rather than activated, using palladium or nickel, points to the requirement of negative charges in nickel deposition. These observations are consistent with the findings of earlier studies, namelyelectrons are required for the progress of an autocatalytic reaction such as electroless nickel plating,¹¹ and holes are required for palladium deposition on silicon by displacement of silicon atoms into the activator solution consisting of fluoride ions.⁹ It is mentioned that, for substrates without any activation, the trends revealed in current-voltage testing could not be discerned from the adhesion vs. doping data. This brings out the utility of using current-voltage testing in combination with adhesion measurements for diagnostic purposes.

We interpret the remaining observed trends in terms of a model of the electroless nickel-polished silicon interface proposed in Fig. 6. This model can be constructed logically from information available in the literature.¹²⁻¹⁶ In our earlier work,¹² we gave an SEM photo of metal islands on the silicon surface at the end of immersion in an activator solution. The presence of the metal was confirmed using EDAX. A conceptual diagram of metal islands acting as nucleation sites is shown in Fig. 6a. On heating to a temperature >200°C, the metal islands react with silicon to forming metal-silicide. Formation of palladium and nickel silicide in this manner, for temperature >200°C, has been discussed in Ref. 13-15. The inverted pyramidal growth of nickel from nucleation islands during electroless plating (see Fig. 6b and c), is inferred from the 2-D model of metal plating given in Ref. 16. Such a growth results from the simultaneous reactions of metal-substrate and metal-metal bonding taking place during plating. Inverted pyramids are formed since the metalmetal bond formation (in the vertical direction) has a higher rate than the metal-substrate bond formation (in the lateral direction). The pyramids coalesce, after an initial growth, to provide a continuous surface. The various observed trends in adhesion and I-V characteristics can be interpreted based on the intermediate layer of nickel or palladium silicide, present on activated silicon substrates, between the plating and silicon.

The higher adhesion due to nickel activation implies that siliconnickel silicide-nickel bond is mechanically much stronger than the silicon-palladium silicide-nickel bond. Because nickel activation involves immersion in an alkaline solution at elevated temperature, it is necessary to investigate the contribution of roughening of the silicon surface due to etching during this immersion, to the adhesion improvement. Alkaline silicon etchants used in MEMS,¹⁷ e.g., KOH and TMAH, etch silicon @ $\sim 1 \ \mu m/min$. In KOH etching,¹⁷ the temperature used is comparable to that used in our nickel plating bath, but the pH 13 used therein is much higher than pH 9 used in our experiments. Thus, the effective molar concentration of the etchant species used in our experiment is \sim 10,000 times lower than that in KOH etching, implying an etching of a few A° only, during the 2 min immersion associated with the activation process. Further, we studied the effect of mild etching of silicon, using an acidic HNO3:HF:H2O etchant (200:1:75) which etches silicon @ ~125 A^0 /min. The plating adhesion due to a 2 min etch instead of nickel activation, prior to electroless plating, was only ${\sim}20\%$ of the value obtained using nickel activation. Both heavily doped and lightly doped, N-type as well as P-type, substrates of 1 cm² area were covered in this study. These observations establish that the improved adhesion from nickel activation is mainly due to the strength of the silicon-nickel silicide-nickel bond and not due to surface roughening during activation.

The resistance associated with nickel silicide layer is higher than that associated with palladium silicide layer, as shown by the higher forward voltage of nickel activated substrates. Palladium activation improves adhesion on all substrates, and in addition, lowers the forward voltage except on N^+ substrates, implying that nickel-palladium silicide-silicon bond has reasonably high mechanical strength on all substrates, and, at the same time, a low resistance except on N^+ substrates.

The rise in forward voltage on N^+ substrates due to palladium activation implies that the resistance of the palladium-silicide layer on these substrates is high. However, the reason for the reduction in forward voltage on P^+ substrates due to nickel activation, in spite of the requirement of electrons in nickel activation, is not clear. These observations are significant enough to merit further investigation for a convincing explanation.

The decrease in plating adhesion with increase in substrate area observed on palladium activated P-type substrates is also observed on unactivated P-type substrates, and is not observed on N-type substrates. So, this observation should be related to the electroless nickel plating and substrate doping, and not to the activation process, and can be explained by the combination of facts, namely, paucity of electrons in a P-type substrate, and the requirement of electrons in electroless plating. Paucity of electrons produces a number of activation sites where the nickel is weakly bonded to palladium-silicide. Weak bonds decide the measured adhesion. As substrate area increases, the possibility of weaker bonds increases, and this reduces the adhesion. Note that, while the palladiumsilcide-silicon bonds at the nucleation sites are uniformly good on substrates where holes are in a majority, and improve adhesion, the nickel-palladium silicide bonds at many sites tend to be weak on these substrates where electrons are in a minority. The simultaneous presence of these factors accounts for the observation on P-type substrates, that palladium activation enhances adhesion of nickel plating to silicon, without eliminating the reduction of adhesion with increase in substrate area.

The decrease in adhesion with plating duration implies generation of stresses in the plated film with increase in plating thickness. Because this has been observed to occur on palladium activated and unactivated substrates, and not on nickel activated substrates, it can be concluded that the structural mismatch at the interface is much less in the case of nickel activation than in the other cases.

Finally, it is pointed out that the scope of our work is limited to the characteristics for as-plated contact, without any post-plating and precharacterization heat-treatment at elevated temperatures capable of altering the nickel-silicon interface. Further, the sintering temperature used during activation did not exceed 400°C. Postplating heating and/or higher sintering temperatures (600-700°C) during activation are essential to lower the high values of contact resistance obtained in our work to practically tolerable limits.³ Without such treatments, the resistance of electroless contacts tends to be higher than those of sputtered contacts, possibly because an oxide layer grows over the substrate area not covered by nucleation sites, due to the aquous nature of the electroless plating solution.¹³ Hightemperature heat-treatment causes the metal and phosphorus present in the electroless deposit to diffuse into silicon (through any oxide barrier), increasing contact area and modifying the surface layer composition, and thus reducing the contact resistance;^{3,13} it also eliminates the effects of variation in plating conditions.³

Conclusion

In this work, the effects of activating polished crystalline silicon with nickel and palladium, on the adhesion and current-voltage characteristics of as-plated electroless nickel are presented and compared. The useful conclusions from this study are the following. Nickel activation occurs by autocatalytic reaction, which requires supply of electrons, and is therefore more effective in reducing forward voltage on N-substrates, as compared to P-type substrates. Palladium activation, on the other hand, occurs by displacement plating reaction, which requires supply of holes; it is most effective on P⁺ substrates and disadvantageous on N⁺ substrates. Nickel activation gives higher adhesion than palladium activation, but a higher for-

ward voltage than even the no activation case, on all but P⁺ substrates. Thus, an improvement in adhesion does not necessarily translate into reduction in forward voltage, due to the resistance associated with the intermediate silicide layer. The palladium silicide formation in the palladium activation step requires a temperature of 200°C as against the 400°C required for nickel silicide formation in nickel activation. Palladium activation is preferable over nickel activation in applications where schottky type contact is required. For ohmic contacts on N⁺ substrates, a low contact resistance is obtained without any activation. However, for ohmic contacts on P⁺ substrates, nickel or palladium activation is necessary to lower the resistance.

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