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Electroless nickel plated contacts on porous silicon

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We have presented the electroless nickel plating technique as a preferred method for making ohmic or rectifying contacts on porous silicon. Nickel, plated by this technique, penetrates the pores and forms contact on an effective area, about 4.5 times the actual area of the sample. High-temperature annealing of the plated metal produced excellent ohmic contacts with porous silicon formed on *n*-type silicon. The properties of this contact are shown to be much superior to that of conventional evaporated and alloyed ohmic contacts made on *p*-type porous silicon of identical characteristics. Contacts made under similar conditions by electroless nickel plating on *p*-type porous silicon, on the other hand, showed good rectifying diode characteristics. The observed electrical properties of electroless nickel contacts are believed to be due to the presence of minute amounts of phosphorous with the plated metal. © *1996 American Institute of Physics.* [S0003-6951(96)04110-6]

Porous silicon (PSi) has emerged as a potential material for making Si optoelectronic devices and integrated circuits. Until now, a variety of photodetectors[1–3] and light emitting diodes[4–9] have been realized using PSi. However the performance of these devices still lack commercial acceptance. The usual problems associated with PSi are the instability of material properties, large resistivity, and difficulty in doing certain process steps such as photolithography.[3] High contact resistances associated with the usual vaccum-deposited metal films may be another source for degrading device performance. Such films tend to make only superficial contacts with the top surface of the porous structure and thereby increase the contact resistance. The true surface area of PSi is known to be very large[10] due to the presence of micropores and, for getting low resistance contacts, it is necessary that these pores be filled by the contact metal.

Electroplating of PSi was previously shown[11] to be a useful alternative for making low resistance contacts to Si. In this case, metal ions penetrated the pores and formed contact on a much larger area. We have used electroless Ni plating[12] as a better choice for this purpose, where no contact lead fabrication is required as in the case of electroplating. Besides, the electroless plating technique offers all the major advantages of electroplating, like selectivity of the surface to be plated and control over plating thickness. Further, we have used the room-temperature electroless Ni plating bath developed by Feldestein,[13] where, by proper choice of the bath ohmic contacts to both *p*- and *n*-type Si can be formed.

PSi was formed by us in an anodic etching bath of 1:2 mixture of HF and ethanol, under a current density of 20–25 mA/cm^2. Both *n*- and *p*-type Si wafers, having resistivities in the range, 1–2 Ω cm and chemically polished on one face, were used. The polished surface was used for PSi formation whereas the other face of the sample was coated with evaporated aluminum films to allow passage of anodizing current.

Electroless plating was done at room temperatures for a duration up to 10 min. Sodium hypophosphite was used as the reducing agent which introduced about 4% phosphorous as impurity with the plated metal. In all cases, along with the porous sample, a polished Si wafer of identical characteristics was placed in the plating bath. This second wafer served as the control sample to monitor the plating rate. Apparently, plating occurred at a much higher rate on the porous surface compared to that on the control sample. This was indicated by the very rapid evolution of hydrogen gas bubbles from the PSi surface. The rate of plating was calculated from the weight gain of the control sample, as the film thickness increased. This parameter was then used to estimate the effective PSi surface area, over which Ni plating took place, as a function of plating time. These data are shown in Fig. 1. As one can see from this figure, the effective plating area is about 4.5 times the actual area of the sample, during the initial phase of plating. As plating proceeded, the effective area reduced and approached the actual area of the sample after long durations of plating. This result can be explained by saying that the plating solution is infiltrating the pores to cause plating on an enhanced surface area. The effect reduced with time as the Ni film grew thicker and the pores got filled up, causing a gradual decrease of the effective area available for plating. It may, however, be noted that only a tiny fraction of the total PSi area, which for our anodizing parameters may be as large as 5000 times the sample area, is being approached by the solution. We believe that the evolution of tiny hydrogen bubbles, as a result of plating reaction, is actually blocking the penetration of the solution deep into

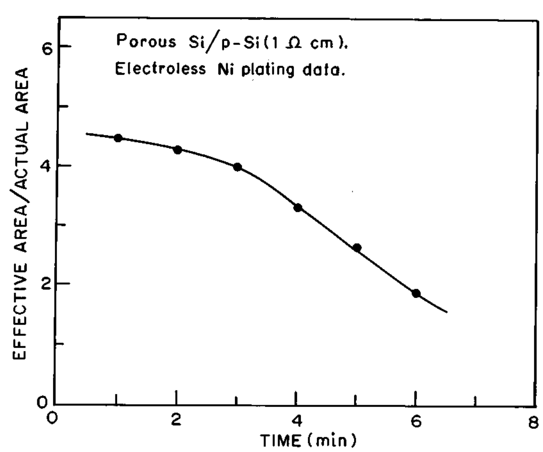

FIG. 1. Effective area of Ni plating on PSi, shown as a function of the plating time.

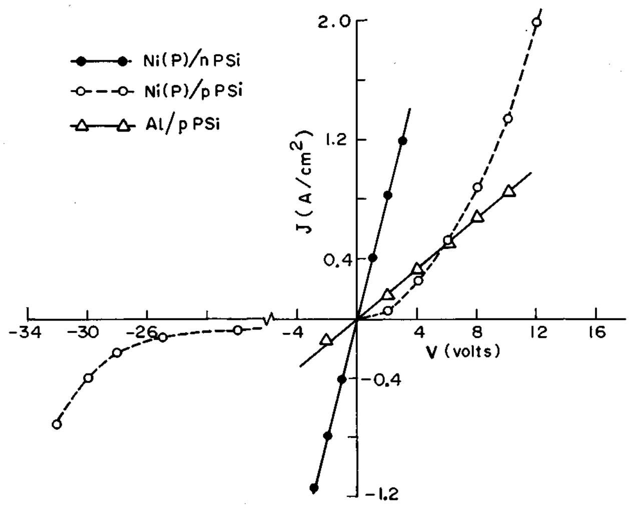

FIG. 2. Current–voltage characteristics of electroless Ni(P) and evaporated Al contacts on PSi.

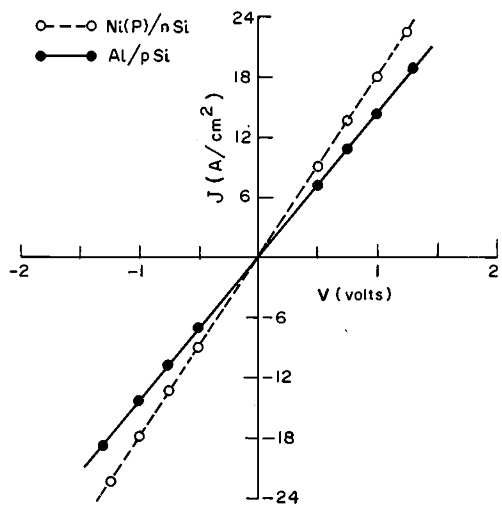

FIG. 3. Current–voltage characteristics of electroless Ni(P) and evaporated Al contacts on polished *n*- and *p*-type Si surfaces, respectively.

the pores. One possible advantage of such blocking effect would be to prevent the metal from contacting the Si surface underneath the porous structure which would otherwise electrically short circuit the porous medium.

In order to check the electrical properties of the contact formed by electroless deposition of Ni(P), thick layers of PSi were grown on one *n*-type and one *p*-type Si wafers using an anodizing time of 20 min. Both the wafers had the same resistivity of 1 Ω cm and their surfaces were prepared in the same manner. Ohmic contact to the back surface of the *n*-type sample was made by plating Ni(P) which was subsequently annealed at 500 °C for 10 min under hydrogen flow. Annealing under such conditions is known to promote diffusion of P into the semiconductor, resulting in a very low resistance ohmic contact with *n*-type Si.[12] Similar annealing was used for the *p*-type sample whose back surface was coated with an evaporated film of Al.

The PSi surfaces for both the samples were coated with electroless Ni(P), deposited for 7–8 min and subsequently annealed under the conditions stated above. Small circular metal dots of 1–2 mm diameter were next defined on the Ni(P) surfaces by mesa etching in a suitable etchant. An identical *p*-type PSi sample was used for making evaporated and annealed Al dot contacts having similar diameters. Figure 2 shows the current–voltage characteristics of all the three types of contacts described above. Both Ni(P)-*n*PSi and Al-*p*PSi contacts show perfectly linear ohmic characteristics. The resistance associated with the Ni(P)-*n*PSi contact is, however, about 5 times smaller than that with the alloyed Al contact with *p*-type PSi. The resistance of the contacts obtained from the slopes of the linear curves, is the sum of the actual contact resistance at the metal–semiconductor interface and the bulk resistance of PSi underneath the contact. In order to check if there is any difference in the former resistance due to the use of different contact materials, we repeated the above experiment with contacts fabricated on polished surfaces of *n*- and *p*-type Si. Figure 3 shows the results. It is clear that Ni(P) on *n*-Si gives a marginally better characteristic compared to that for Al on *p*-type Si. Thus the observed lowering of contact resistance associated with Ni(P) on *n*-type PSi is almost entirely due to the increase in area coverage by the metal film.

Finally, we note that the electrical contact of Ni(P) on *p*-type PSi gives an excellent diodelike behavior which may be attributed to the diffusion of P from Ni(P) into PSi during high-temperature annealing.

In conclusion, the electroless Ni plating technique can be used for making large area, low resistance electrical contacts with PSi. The measured contact resistances associated with such contacts are much smaller than corresponding contacts made by the conventional evaporated Al films. It is also possible to use the plating technique to fabricate stable *p-n* diodes with PSi.

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