The fabrication of Schottky-barrier solar cells by electroless nickel plating

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(Received 2 October 1978; accepted for publication 28 February 1979)

Fabrication of Schottky-barrier solar cells by electroless nickel plating can be recognized as a practical approach because cells made by this method are of lower cost, have good adhesion to the surface, higher barrier potential height, and lower reflectivity of light as compared with those of the vacuum-evaporated devices. No expensive equipment, such as a vacuum evaporator or high-temperature diffusion oven, is needed for this manufacture.

PACS numbers: 72.40.+w, 73.30.+y, 84.60.Jt

Although electroless nickel plating is a well-known technique for implementing an intermediate metallization layer to a semiconductor, applying this process for fabrication of Schottky-barrier contacts is still unreported. We found that the use of electroless plating can be recognized as a practical approach because solar cells fabricated by this method are of lower cost, have good adhesion to the surface, higher barrier potential height, and higher light absorption when compared with those of the vacuum-evaporated devices.

There are several excellent reviews on electroless nickel plating. For plating n-type silicon, the Brenner method is used. The composition of the plating bath is nickel chloride (NiCl₂, 6H₂O), 30 g/l; ammonium citrate [NH₄]₂HC₂H₂O, 65 g/l; and ammonium chloride (NH₄Cl) 50 g/l. The reducing agent, sodium hyposulfite (Na₂S₂O₄·5H₂O), 10 g/l, is added slowly with agitation. The final solution is then filtered. Wafers are given a chemical etching (HNO₃: 44%; HF: 18%; H₂O: 38%). Immediately prior to plating, the specimens are given a 1-min dip in HF (48%) and a thorough rinsing with deionized water. The edges and one side of the silicon slab are painted with insoluble (acetone based) ink. The solution is adjusted to pH 8–10 before use with ammonium hydroxide by adding it dropwise until the solution changes color from green to blue due to complex formation. The rate of deposition depends primarily on the temperature of operation, the ammonia concentration, the surface pretreatment and cleanliness, and the purity of the solution. Deposition is continued for a period of 20 min in the solution operated at 90 °C. Usually this produces a dull-white covering on the exposed surfaces. The mask paint is removed with acetone and then rinsed in distilled water. The wafer is annealed in nitrogen atmosphere at 500 °C for 1 h. The diffused wafers are quickly quenched to room temperature upon removal from the furnace to prevent precipitation and out-diffusion of the nickel atoms. The cells are masked on the plated-diffused side and on the cell edges and covered with tape or resin. The SiO₂ layer produced during prior sintering is removed in HF. The exposed silicon is then plated for a Schottky contact with the nickel bath operating at 70 °C at a deposition rate of 70 Å/min. There is an optimum thickness of the barrier metal which is a compromise between obtaining high transmission of light and a low series resistance through the metal film. The maximum short-circuit current Iₛ is obtained after deposition for about 3 min.

To make a metallized layer (Ohmic contact) for p-type silicon, the plating solution containing phosphorus cannot be used. As an alternative we tried using a borohydride-based bath to dope the silicon. One of the successful plating solutions included ammonium hydroxide as the complexing agent. The bath is prepared by dissolving nickel chlorides, 36 g/l, and ammonium hydroxide (28% NH₃), 132 ml/l, in distilled water. The solution is filtered, and the bath temperature kept at 40 °C. The cleaned and etched silicon wafer is activated by dipping in sodium borohydride (NaBH₄), 2.2 g/l, solution and then dropped into the nickel chloride solution. A few drops of sodium borohydride solution is added slowly, with agitation, to the nickel salt solution just before deposition. Too rapid or too much addition of borohydride would cause precipitation of nickel hydroxide, making deposition impossible.

The C-V characteristics measured by the phase-locked-loop method. The barrier heights are Vₚ = Vₚ + kT/q − Δφ = 0.48 V + 0.26 V + 0.0258 V − 0.0179 V = 0.74 V for the evaporated device and Vₚ = 0.83 V for the electroless plated device.
loop method\textsuperscript{11} is shown in Fig. 1. The Schottky-barrier height for \textit{n}-type material can be written as

\[ \phi_{Bn} = V_i + V_n + kT/q - \Delta \phi, \]

where \( V_i \) is the intercept voltage from the \( 1/C^2 \)-vs-\( V \) plot, \( V_n = E_c - E_F \), and \( \Delta \phi \) is the image potential lowering. The barrier height \( \phi_{Bn} = 0.74 V \) of samples prepared by the vacuum-deposition method is comparable to that of other reported data.\textsuperscript{12} The barrier height of the plated diode is 100 mV higher than that of the vacuum-deposited diode. This might be due to the activation of the surface by hypophosphite, polyphosphite, chloride, and, possibly, mainly from the formation of Si-H bonds near the surface. The interface states can be partially removed because of the reactions of hydrogen atoms with the incompletely bonded silicon atoms to form the Si-H bond,\textsuperscript{13} i.e., removing the so-called “dangling bonds” during the plating process. For an \textit{n}-type semiconductor, at a doping of \( N_D < 10^{18} \text{ cm}^{-3} \), the barrier height\textsuperscript{14} is approximated by

\[ \phi_{Bn} = \frac{\epsilon_1}{\epsilon_i + q\delta D_s} \phi_m + c_s, \]

where \( \epsilon_1 \) is the permittivity of the interfacial layer of thickness \( \delta \), \( \epsilon_i \) is the work function of metal, \( c_s \) is a constant, and \( D_s \) is the surface-state density. Decreasing the surface states would increase the barrier height.

Ion backscattering (Fig. 2) indicates that the phosphorus content of the deposit is about 7\% at a batch of \( \rho \text{H} = 9.5 \) and increases as the \( \rho \text{H} \) decreases. An analysis of electron and x-ray-diffraction patterns shows that the as-plated deposits are supersaturated solutions of phosphorus dissolved in finely crystalline nickel. Heat treatment at 400°C results in precipitation of an intermetallic Ni,P phase and nickel grain growth.\textsuperscript{15} After annealing, as can be seen from Fig. 3, the collapse of the steps on the high-energy sides of P and Si clearly indicates that P and Si have reacted and the Si atoms have partly migrated into the Ni,P alloy. Therefore, a higher donor layer is formed at the back surface (or \( n^+ \) heterojunction), resulting in a higher collecting efficiency of the minority carriers as a result of the back surface field.

The \( I-V \) characteristics of the as-plated and as-evaporated samples are compared at different illuminations, as shown in Fig. 4. The plated Schottky solar cells show higher leakage current because of the precipitation of nickel atoms along the dislocation during rapid quenching from a high temperature.\textsuperscript{11} They also show poorer front-to-back contact leakage because more impurities are added during plating. Spectroscopic measurements show that there are no differences in reflectivity as a function of wavelength except that the reflectivity of the as-plated sample is 15\% lower than that of the evaporated sample.

\[ \text{FIG. 2. Backscattering spectra of the electroless nickel-plated } \textit{n}-\text{type silicon at bath solutions of } \rho \text{H} = 8 \text{ and } \rho \text{H} = 9.5 \text{, respectively, in different deposited thickness. The arrows indicate the energy corresponding to scattering from atoms at the front edge. The phosphor content is obtained by taking the ratio } N_f/N_m = (V_f/V_m)(S_f/S_m)(\sigma_f/\sigma_m), \text{ where } V \text{ is the total backscattered yield, } S \text{ is the backscattering energy loss parameter, and } \sigma \text{ is the Rutherford cross section.} \]

\[ \text{FIG. 3. Backscattering spectra of the virgin annealed samples. The front edge of the Ni signal is shift below its surface peak, after annealing, because of the presence of oxide and segregated impurities on the top.} \]

\[ \text{FIG. 4. The } I-V \text{ characteristics of the electroless plated and the vacuum-evaporated Schottky-barrier solar cells at several levels of illuminating light. A: dark; B 100 mW/cm}^2; \text{ C: 140 mW/cm}^2; \text{ with an unfiltered tungsten quartz halogen lamp.} \]
Laser irradiation of silicon containing misfit dislocations

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(Received 13 November 1978; accepted for publication 28 February 1979)

Silicon containing misfit dislocations caused by ion implantation and thermal annealing were irradiated with a scanning Q-switched Nd-YAG laser. It was found that misfit dislocations can be removed completely. It was established that this removal is thermally stable. Evidence for a melting-resolidification mechanism was observed. The thermally stable removal of misfit dislocations is discussed in terms of this mechanism.

PACS numbers: 79.20.Ds, 61.70.Tm, 61.70.Jc, 81.40Ef

The method of laser annealing ion-implanted Si has strong capabilities for removing the damage caused by ion implantation.1 This has been extensively verified for ion-implanted Si with Rutherford backscattering spectrometry (RBS) and transmission electron microscopy (TEM).2-4 In the case where an amorphous layer is formed by the implantation of dopant ions, it is often found that after the epitaxial regrowth of the amorphous layer the concentration of dopant ions on lattice positions exceeds the solid solubility. However, this situation is found to be thermally unstable.1 One may wonder whether such a nonequilibrium situation may also occur regarding the removal of damage and, in particular, in the case where the implantation conditions are such that after thermal annealing misfit dislocations are formed. Misfit dislocations are often found after the thermal annealing of heavily doped Si. They are considered to be due to stress caused by a difference in ionic radii of the dopant and host material.4 The well-known misfit dislocations in Si contain a high concentration of P, which has a smaller ionic radius than Si (P: 0.110 nm, Si: 0.117 nm). It is also known that the occurrence of these misfit dislocations can be suppressed by adding dopant ions which have somewhat bigger radius than Si, such as Sn or Ge.6 Evidently, these dopant ions induce stress compensation. From about considerations one may derive the supposition that if misfit dislocations can be removed by laser irradiation, a thermally unstable situation may exist, that is, a subsequent heat treatment will bring them back again. This would limit the practical application of laser annealing as a method for removal of implantation damage. Therefore, we have studied this aspect in more detail.

We investigated the influence of laser irradiation on misfit dislocations which are formed by implanting P ions at a dose of 10^16 ions cm^-2 and at an energy of 50 keV into <111>-oriented Si and by applying a subsequent thermal annealing process at 1100°C for 40 min in N2. These samples containing misfit dislocations were irradiated with a focused scanning Nd-YAG Q-switched laser operating in the TEM00 mode. Specifications of this setup are as follows: repetition frequency 4 kHz, pulse length 180 nsec, beam spot size ~ 50 μm, X-Y table with a scanning velocity of 7.5 cm/sec, and a X-Y-table size of 24, 30, 36, and 41 MW cm^-2. Some of the irradiated samples were subsequently annealed...