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## Electrochemical fabrication of *n*-Si/Au Schottky junctions

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We report on the electrochemical deposition of gold films onto *n*-type silicon. Gold deposition occurs through progressive nucleation and diffusion limited growth. A high density of gold nuclei was obtained by using a short potential pulse to -1.6 V(Ag/AgCl), and subsequent growth was performed at about -1.1 V(Ag/AgCl) where the growth rate is kinetically limited. Transmission electron microscopy showed that high quality, continuous gold films were formed with an average grain size on the order of 50-70 nm. The electrical properties of the electrochemically deposited Si/Au Schottky junctions are comparable to junctions prepared by evaporation or sputtering techniques. © 1998 American Institute of Physics. [S0003-6951(98)01948-2]

Electrochemical deposition of metals and alloys onto metallic substrates plays an important role in many modern technologies. For example, in the electronics industry electrochemical and electroless deposition are widely used for applications such as copper printed circuit boards, throughhole plating, multilayer read/write heads, and thin film magnetic recording media.<sup>1</sup> In contrast, the electrochemical deposition of thin, continuous metal films onto silicon has been largely overlooked despite the technological importance for applications such as Schottky junctions and metallization.

The thermodynamics and kinetics of metal deposition on semiconductors are dependent on the accessible energy levels in the semiconductor and solution. Figure 1 illustrates possible mechanisms for metal deposition on a semiconductor surface; for convenience the metal ion is considered as an acceptor state with a temporal distribution of energy levels.<sup>2-5</sup> A metal/metal ion redox couple with a sufficiently negative equilibrium potential (e.g., a transition metal) has acceptor levels that have a large overlap with the conduction band edge. If the surface electron concentration in the conduction band is sufficiently high, electrons can be transferred to the metal ion in solution resulting in deposition of the metal. The deposition rate is dependent on the band bending and can be controlled by the applied potential. For the case of a metal/metal ion couple with a positive equilibrium potential (e.g., a noble metal), where the acceptor states overlap with the valence band of the semiconductor, deposition takes place by hole injection into the valence band. When the positions of the band edges are fixed, the deposition rate is expected to be independent of applied potential. In this case, deposition can occur under open circuit conditions as long as a suitable hole acceptor is present in solution. However, hole injection often leads to oxidation of the semiconductor resulting in either the formation of an oxide layer or dissolution of the semiconductor. Based on these considerations, deposition via the conduction band is preferred since the growth mechanism and, hence, the properties of the deposited films can be controlled by means of the applied potential.

The mechanism of deposition can be changed by tuning the position of the band edges or the energy of the acceptor levels in solution. For (100) oriented *n*-type silicon (4  $\Omega$  cm) in a pH 0 solution the conduction band edge  $(E_{CB})$  and valence band edge  $(E_{\rm VB})$  at the surface are located at about -0.6 V (Ag/AgCl) and 0.5 V(Ag/AgCl), respectively.<sup>6</sup> The equilibrium potential for the  $AuCl_{4}^{-}/Au$  couple is 0.78 V(Ag/AgCl),<sup>7</sup> so there is expected to be significant overlap between the valence band and the acceptor levels. This is confirmed by the observation that gold deposition from  $AuCl_{4}^{-}$  in 1 M HCl+1 M HF solution occurs under open circuit conditions on both n- and p-type silicon. However, the films were highly stressed and had poor adhesion. In pH solution, the band edges are shifted to  $E_{\rm CB}$ 14  $\approx -1.4 \text{ V}(\text{Ag/AgCl})$  and  $E_{\text{VB}} \approx -0.3 \text{ V}(\text{Ag/AgCl}).^{8}$  The equilibrium potential for Au(CN)<sub>2</sub><sup>-</sup> in pH 14 solution is about -0.82 V(Ag/AgCl),<sup>7</sup> so that the energy levels of the gold acceptor states are expected to overlap with the conduction band. In this case, gold deposition is not observed under open circuit conditions, indicating that there is no overlap of gold acceptor states with the valence band. In addition, gold deposition on *p*-type silicon can only be achieved under illumination, confirming that the deposition mechanism is electron transfer from the conduction band.



FIG. 1. Energy band diagram illustrating possible mechanisms of metal deposition on an n-type semiconductor; the energy levels of the oxidized species are shown as a Gaussian distribution. Deposition of a metal from a metal/metal ion couple with a negative equilibrium potential,  $E_{O/R}^1$ , takes place via electron transfer from the conduction band to the solution, and deposition from a metal/metal ion couple with a positive equilibrium potential,  $E_{O/R}^2$ , occurs through hole injection into the valence band.

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FIG. 2. Voltammograms for (100) oriented *n*-type silicon (4  $\Omega$  cm) in 1 M KCN solution at 14 pH with (a) 0 and (b) 50 mM KAu(CN)<sub>2</sub>. The scans were started at the OCP, and the scan rate was 10 mV s<sup>-1</sup>.

Figure 2 shows a cyclic voltammogram for (100) oriented *n*-type silicon (4  $\Omega$  cm) in 1 M KCN solution, adjusted to pH 14 with KOH, with and without 50 mM KAu(CN)<sub>2</sub>. The experiments were performed using a conventional three electrode cell with a Ag/AgCl (3 M NaCl) reference and a platinum counter electrode. At this pH, the silicon surface is hydrogen terminated and is stable under open circuit conditions and at potentials negative with respect to the open circuit potential (OCP).<sup>9,10</sup> Consequently, the formation of an oxide during deposition can be avoided. The voltammogram in the gold solution shows a characteristic peak at about -1.30 V(Ag/AgCl) due to gold deposition followed by a sharp increase in the current at -1.65 V(Ag/AgCl) due to catalyzed hydrogen evolution on the gold clusters. On the reverse scan, gold deposition is observed up to -1.0 V(Ag/AgCl) indicating that an overpotential of about 0.3 V is required for nucleation. The reverse scan does not show a stripping peak which, in the absence of valence band holes, shows that a high barrier n-Si/Au Schottky junction has been formed.

Figure 3 shows a series of current transients for potential steps from the OCP to various potentials for gold deposition from 50 mM  $Au(CN)_2^-$  in 1 M KCN at pH 14. The transients



FIG. 3. Current response to potential steps from -1.1 V (Ag/AgCl), where no deposition takes place, to (a) -1.6 (Ag/AgCl), (b) -1.5 (Ag/AgCl), and (c) -1.4 V (Ag/AgCl). The inset shows the transients replotted in dimensionless form: ( $\Box$ ) -1.6 (Ag/AgCl), ( $\bigcirc$ ) -1.5 (Ag/AgCl), and ( $\triangle$ ) -1.4 V(Ag/AgCl). The theoretical curves for instantaneous (dashed) and progressive nucleation (solid) with diffusion limited growth are also shown.



FIG. 4. Cross-sectional TEM image of an electrochemically deposited gold film on n-type Si(100).

are characteristic of three dimensional nucleation followed by diffusion limited growth.<sup>11</sup> The inset of Fig. 3 shows the transients replotted in dimensionless form, along with the theoretical curves for instantaneous and progressive nucleation.<sup>12,13</sup> The transients show excellent agreement with the progressive nucleation model. The diffusion coefficient of Au(CN)<sub>2</sub><sup>-</sup> can be obtained from the product  $i_m^2 t_m$  [where  $i_m^2 t_m = 0.2598(zFc)^2D$ ],<sup>12,13</sup> resulting in a value of 1.5  $\times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>, close to values reported in the literature.<sup>14</sup> The diffusion coefficient can also be obtained from the current decay at long times from the Cottrell equation for linear diffusion to a planar surface, which resulted in a value of 2  $\times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.

Based on these results, the experimental conditions for the deposition of high quality, continuous gold films on silicon can be determined. The general approach is to provide a potential pulse at negative potentials where a high density of nuclei is formed, followed by growth at more positive potentials under charge transfer or mixed charge transfer/mass transport control. Growth under charge transfer control is necessary in order to prevent dendritic growth of the nucle-



FIG. 5. (a) Mott–Schottky plot and (b) current density  $(A \text{ cm}^{-2})$  vs a potential curve on a semilogarithmic plot for an *n*-Si/Au Schottky junction prepared by electrochemical deposition.

ated clusters.<sup>15,16</sup> The gold films deposited using this method were bright and exhibited good adhesion to the silicon surface.

Figure 4 shows a cross-sectional transmission electron microscopy (TEM) image of an electrochemically deposited gold film on n-Si(100). We note that the delamination of the gold film in the image is due to sample preparation. The film was deposited using an initial potential pulse to -1.65V(Ag/AgCl) for 50 ms followed by growth at -1.12 V(Ag/ AgCl) for 200 s. The total charge passed was  $0.1 \text{ C cm}^{-2}$ , corresponding to a film thickness of 100 nm (assuming 100% efficiency), close to the average film thickness of 90 nm obtained from TEM images. The TEM image reveals the presence of stacking faults which is often found for gold deposition. The gold film is continuous with equiaxed grains with an average size on the order of 50-70 nm. The grain size is expected to be determined by the nucleus density since growth of the nuclei continues until they coalesce resulting in a continuous film. The average grain size of 60 nm corresponds to a nucleus density of  $2.8 \times 10^{10}$  cm<sup>-2</sup>. This is in good agreement with scanning electron microscopy images of silicon surfaces after deposition of about 5 mC cm<sup>-2</sup> of gold (20 equivalent monolayers) which revealed a nucleus density of about  $2 \times 10^{10}$  cm<sup>-2</sup>.

The electrical properties of the electrochemically prepared Si/Au junctions were characterized by measuring the barrier height and ideality factor of the junctions. Figure 5(a) shows a plot of  $C^{-2}$  (where *C* is the measured capacitance) versus the applied bias. The plot is linear and the intercept with the potential axis is -0.51 V, which leads to a barrier height of 0.79 eV. Figure 5(b) shows the forward current versus the applied bias on a semilogarithmic plot corrected for the reverse bias current.<sup>17</sup> The plot is linear over about five orders of magnitude and from the slope of the current– voltage curve the ideality factor was determined to be 1.2 which shows that these junctions are nearly ideal.<sup>17</sup> The saturation current,  $j_0$ , was determined to be  $2.8 \times 10^{-7}$  A cm<sup>-2</sup> resulting in a barrier height of 0.80 eV. The values for the barrier height obtained by the two different methods are in excellent agreement indicating the absence of either an interfacial layer or a high density of electrically active surface states. These characteristics are comparable to junctions obtained by sputter deposition or evaporation.<sup>17</sup>

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