

# Fabrication of minority-carrier-limited *n*-Si/insulator/metal diodes

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A photoelectrochemical anodization technique has been used to fabricate *n*-Si/insulator/metal (MIS) diodes with improved electrical properties. MIS structures fabricated with Au have provided the first experimental observation of a solid-state *n*-Si surface barrier device whose open circuit voltage  $V_{oc}$  is controlled by minority-carrier bulk diffusion/recombination processes. For these diodes, variation of the minority-carrier diffusion length and majority-carrier dopant density produced changes in  $V_{oc}$  that were in accord with bulk diffusion/recombination theory. Additionally, the variation in  $V_{oc}$  in response to changes in the work function of the metal overlayer indicated that these MIS devices were not subject to the Fermi level pinning restrictions observed for *n*-Si Schottky structures. X-ray photoelectron spectroscopic characterization of the anodically grown insulator indicated  $8.2 \pm 0.9 \text{ \AA}$  of a strained SiO<sub>2</sub> layer as the interfacial insulator resulting from the photoanodization process.

Although numerous studies of the semiconductor/liquid interface have addressed the design of efficient photoelectrochemical solar cells,<sup>1,2</sup> little attention has been devoted to the application of photoelectrochemistry to improve the performance of solid-state devices. Deposition of ultrathin dielectric layers is crucial to the fabrication of optimized metal-insulator-semiconductor (MIS) solar cells, chemically sensitive field-effect transistors, and tunnel-oxide based devices,<sup>3</sup> and photoelectrochemical techniques might afford controlled surface oxidation processes that are unavailable with thermal oxidation or other wet chemical methods. In particular, for *p*-type Si-based solar cells, Green and co-workers have obtained bulk diffusion/recombination limited performance with thermal oxidation techniques,<sup>4</sup> and have fabricated minority-carrier MIS systems which yield some of the highest open circuit voltages ( $V_{oc}$ ) reported to date for any Si solar cell.<sup>4,5</sup> However, minority-carrier dominated behavior has not been reported for *n*-type Si-based MIS systems, because conventional oxidation techniques have resulted in *n*-Si/oxide/metal interfaces with large majority-carrier thermionic emission currents.<sup>6,7</sup> We report the use of photoelectrochemical oxidation techniques to prepare minority-carrier MIS systems with *n*-Si substrates, and report the preparation of *n*-Si MIS diodes that exhibit different electrical device properties with metals of different work functions.

The method of junction formation used in this work was based on the photoelectrochemistry of *n*-Si in alcohol solutions.<sup>8</sup> We have previously demonstrated that *n*-Si/methanol interfaces can produce liquid junctions which yield  $V_{oc}$  values in agreement with bulk diffusion/recombination theory.<sup>8a</sup> This system yields the theoretical  $V_{oc}$  value of 635 mV for 0.2  $\Omega$  cm *n*-Si samples at 20 mA/cm<sup>2</sup> photocurrent density, and more highly doped samples have produced photovoltages in excess of 670 mV at 300 K (at 20 mA/cm<sup>2</sup> photocurrent density) without any back surface field action.<sup>8b</sup> The high quality of this Si/liquid interface prompted us to apply these photoelectrochemical techniques to the for-

mation of *n*-Si based MIS devices.

Device fabrication involved exposure of a HF etched, (100) oriented *n*-Si sample (typically 0.05–0.5 cm<sup>2</sup> in exposed area) to polychromatic illumination in a methanol solution which contained 50 mM of dimethylferrocene, 5mM of dimethylferricinium (BF<sub>4</sub><sup>-</sup> or Cl<sup>-</sup>), and 1.0 M of LiClO<sub>4</sub>. The Si sample was maintained under potentiostatic control using conventional electrochemical cells and potentiostats,<sup>8b</sup> but dry, anaerobic conditions were not required for the success of the procedure. Short circuit photocurrent densities for separate runs varied from 16–20 mA/cm<sup>2</sup> depending upon the mass transport limit for the particular cell configuration, but in all cases, the photocurrent density was set to be 1–3 mA/cm<sup>2</sup> less than the mass transport limit for dimethylferrocene oxidation. After several potential scans of the *n*-Si electrode from short circuit to the open circuit potential, enough LiOCH<sub>3</sub> was added from a stock solution (1.0–2.5 M LiOCH<sub>3</sub> in methanol) to make the cell solution 0.02–0.08 M in methoxide ion. The *n*-Si electrode was then maintained under potentiostatic control at short circuit relative to the equilibrium solution potential of a Pt reference electrode in the cell solution. The desired oxide thickness was conveniently indicated by a decline in  $V_{oc}$  of 120 mV from its initial value (usually requiring 60–100 min of electrolysis at short circuit). This oxidation required up to 100 min, since the current efficiency for oxide formation is small relative to that for dimethylferrocene oxidation.<sup>8a,b</sup> A 10%–15% decrease in short circuit photocurrent and a degradation of the fill factor was observed to occur concurrently with the drop in  $V_{oc}$ . After overlayer growth, the *n*-Si sample was thoroughly rinsed with CH<sub>3</sub>OH solvent, dried under nitrogen, and transferred to a filament evaporation system. A semitransparent metal film (100–125  $\text{\AA}$ ) was then deposited by thermal evaporation of > 99.99% pure metal from a tungsten filament under a base pressure of  $< 8 \times 10^{-6}$  Torr. The properties of the resulting MIS devices with a series of different barrier metals were then investigated by light *I*-*V*, dark *I*-*V*, and differential capacitance versus voltage techniques.

Figure 1 displays the improvement in *I*-*V* behavior of *n*-

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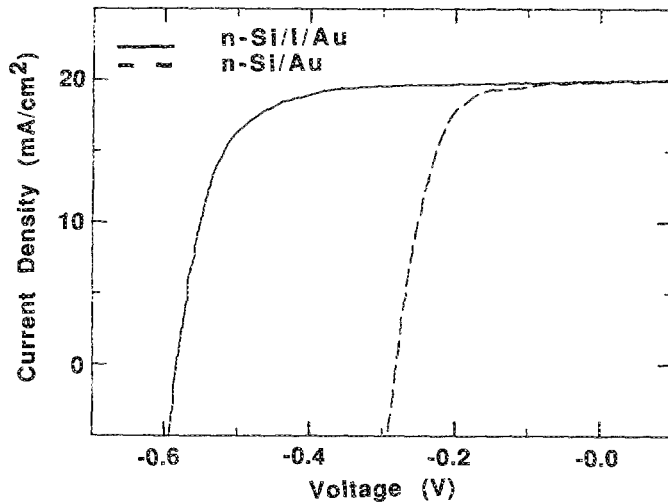


FIG. 1. Current-voltage properties under illumination of an *n*-Si/Au Schottky diode (dashed line) and of an *n*-Si/I/Au MIS (solid line) device at 25 °C (negative voltage is forward bias). The illumination intensities were adjusted to yield short circuit photocurrent densities of 20 mA/cm<sup>2</sup>. The substrate material had a resistivity of 1.08 Ω cm.

Si/Au junctions after photoelectrochemical treatment, as compared to the behavior of *n*-Si/Au Schottky barriers. The photovoltage for the latter device, 0.29 V, is in agreement with expectations based on thermionic emission over a barrier height of 0.80 V for the *n*-Si/Au interface.<sup>3a,5a</sup> In contrast, the 0.58 V  $V_{oc}$  value obtained after anodization of this 1.08 Ω cm *n*-Si sample (370 μm thickness, effective hole diffusion length = 185 μm) indicates that the majority-carrier overbarrier recombination current had been suppressed in this system. The increased  $V_{oc}$  is in accord with a bulk diffusion/recombination process<sup>3a,5a,8a</sup> as expressed by Eq. (1):

$$V_{oc} = (kT/q) \ln(J_{ph} L_p N_D / q D_p n_i^2), \quad (1)$$

where  $J_{ph}$  is the photocurrent density,  $N_D$  is the dopant density,  $L_p$  is the effective minority-carrier diffusion length,  $D_p$  is the minority-carrier diffusion coefficient, and  $n_i$  is the intrinsic carrier concentration. Table I displays the correlation between theoretical open circuit voltages [based on Eq. (1)] and experimentally measured open circuit voltages for Au MIS devices fabricated on *n*-Si samples with varying dopant

TABLE I. Variation in open circuit voltage ( $V_{oc}$ ) for *n*-Si/I/Au devices. Theoretical voltages were calculated from Eq. (1), taking  $n_i = 1.45 \times 10^{10}$  cm<sup>-3</sup> (Ref. 3). All open circuit voltages were measured with W-halogen irradiation sufficient to provide short circuit photocurrent densities of  $20 \pm 2$  mA/cm<sup>2</sup> at 298 K. The typical variation in  $V_{oc}$  among samples of the same resistivity and  $L_p$  was 0.02 V.

Resistivity (Ω cm)	Effective hole diffusion length $L_p$ (μm)	$V_{oc}$ (theory) (V)	$V_{oc}$ (exptl.) (V)
0.24	195	0.63	0.62
0.77	200	0.59	0.60
1.08	185	0.58	0.58
1.35	175	0.57	0.57
1.5	200	0.57	0.57
1.59	13	0.50	0.50

densities and hole diffusion lengths. The  $V_{oc}$  value of 0.62 V obtained with the 0.24 Ω cm *n*-Si sample is much larger than the 0.45–0.54 V values reported for previous *n*-Si based MIS devices at comparable injection levels.<sup>3,5–7</sup> The bulk recombination limited  $V_{oc}$  implies that, even at forward biases of 0.5–0.7 V with relatively low hole injection current densities, these MIS systems exhibit a ratio of hole injection current to electron injection current which is greater than 1.0 for all dopant densities and bulk lifetimes studied. This behavior contrasts with thermally oxidized *n*-Si MIS devices, in which Si samples with much higher hole injection current densities only exhibited hole/electron injection ratios of  $10^{-3}$ – $10^{-2}$  at forward biases of 1 V.<sup>7b</sup>

The open circuit voltages of these MIS systems fabricated on 1.08–1.7 Ω cm *n*-Si with a series of metals are presented in Table II. Substantial frequency dispersion in the differential capacitance versus voltage plots generally prevented a rigorous measurement of the barrier heights using the  $1/C^2$  vs  $V$  method, thus open circuit voltages are reported in Table II. For comparison, the open circuit voltages for analogous *n*-Si/M Schottky diodes were independently measured and have been included in the data set of Table II. The MIS systems exhibited a strong correlation of  $V_{oc}$  with the work function of the metal, as would be expected from the ideal Schottky barrier model. For instance, high work function metals such as Au, Pd, and Pt yielded MIS devices with larger  $V_{oc}$  values than Schottky contacts, whereas low work function metals produced lower  $V_{oc}$  values in the MIS structures than in the corresponding *n*-Si/M Schottky contacts.

Several experiments were performed with Au contacts in order to identify the chemical constituents necessary for successful MIS fabrication. Immersion of *n*-Si samples into the electrolyte in the presence of illumination, but with no faradaic current flow, yielded  $V_{oc}$  values of only 0.36 V, at photocurrent densities of 10–20 mA/cm<sup>2</sup>, after deposition of

TABLE II. Comparison of  $V_{oc}$  for *n*-Si/metal contacts before and after photoelectrochemical anodization.<sup>a</sup>

Metal	Work function <sup>b</sup> (eV)	<i>n</i> -Si/M $V_{oc}$ (V)	<i>n</i> -Si/I/M $V_{oc}$ (V)
Pt	5.6 ± 0.1 <sup>c</sup>	0.36	0.58
Pd	5.5 ± 0.1 <sup>c</sup>	0.24	0.58
Au	5.1 ± 0.1 <sup>c</sup>	0.29	0.58
Ag	5.1 ± 0.2 <sup>d</sup>	0.25	0.52
Rh	5.0 <sup>e</sup>	0.30	0.55
Co	5.0 ± 0.1 <sup>c</sup>	0.18	0.44
Cu	4.7 ± 0.1 <sup>c</sup>	0.06	0.38
Ni	4.6 ± 0.1 <sup>d</sup>	0.10	0.35
Cr	4.5 ± 0.2 <sup>c</sup>	0.09	0.00
Al	4.1 <sup>d</sup>	0.24	0.00

<sup>a</sup>Substrates were *n*-Si (100) oriented samples of either 1.08 Ω cm or 1.7 Ω cm resistivity. The  $V_{oc}$  values were measured with W-halogen irradiation sufficient to provide short circuit photocurrent densities of  $20 \pm 2$  mA/cm<sup>2</sup>. The random variation in the  $V_{oc}$  values was typically  $\pm 0.02$  V.

<sup>b</sup>Where available, work functions for the polycrystalline metal on SiO<sub>2</sub> are listed.

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<sup>d</sup>Reference 3a.

<sup>e</sup>B. E. Niewenhuys, R. Bouman, W. H. M. Sachtler, Thin Solid Films 21, 51 (1974).

a Au overlayer. Additionally, anodizations of *n*-Si in CH<sub>3</sub>OH performed without the simultaneous presence of anodic photocurrent, LiClO<sub>4</sub>, CH<sub>3</sub>O<sup>-</sup> (either generated electrochemically at the cathode or added chemically), dimethylferrocene, and dimethylferricinium failed to produce  $V_{oc}$  values with Au overlayers of greater than 360 mV. For example, samples that were maintained at short circuit current densities of 12–16 mA/cm<sup>2</sup> for 12–24 h, but without exposure to methoxide ion, yielded  $V_{oc}$  values of 0.34–0.38 V upon Au evaporation. These samples displayed peaks in the Si(2*p*) region of the x-ray photoelectron spectrum (XPS) indicating the presence of only  $3.1 \pm 0.4 \text{ \AA}$  of a strained SiO<sub>2</sub> layer<sup>9</sup> [BeV = 103.85 relative to the Si(2*p*<sub>3/2</sub>) component of the Si substrate line at 99.70 BeV] on the silicon surface.

In contrast, XPS analysis of Si surfaces that produced satisfactory MIS behavior revealed the presence of  $8.2 \pm 0.9 \text{ \AA}$  of a strained SiO<sub>2</sub> layer. A wide scan XPS analysis of samples that had been removed from the anodization solution and rinsed with CH<sub>3</sub>OH revealed that approximately  $4.9 \pm 1.5 \text{ \AA}$  of a ferricinium compound was on the surface, as indicated by the presence of a low spin Fe(III) compound, and also revealed an approximately equal amount of fluoride ion. However, the presence of Fe and F was not necessary to obtain the desired MIS device behavior, as evidenced by the high  $V_{oc}$  values of 0.56–0.58 mV that were obtained for Au MIS devices fabricated on 1.3 Ω cm *n*-Si samples that were rinsed with 0.016 M HCl(aq) prior to the metal evaporation step. Such acid rinsed samples exhibited significantly reduced XPS peaks attributable to Fe ( $0.8 \pm 0.2 \text{ \AA}$ ) and F ( $0.8 \pm 0.2 \text{ \AA}$ ), but did display the  $8.2 \pm 0.9 \text{ \AA}$  of strained SiO<sub>2</sub> present in the other anodized *n*-Si samples. Thus, the important factor for MIS device fabrication is that the electrochemical process allows reproducible growth of ultrathin SiO<sub>2</sub> films, and that these oxide films are sufficiently uniform to prevent direct metal/Si contacts and are sufficiently nonporous to prevent interdiffusion of metal to the Si surface during the subsequent thermal metal deposition step.

In summary, we have shown that photoelectrochemical anodization can produce controllable amounts of oxide coatings that lead to novel *n*-Si MIS device properties. These MIS devices display improved  $V_{oc}$  values and exhibit an improved response to the work function of the contacting metal phase. A similar process may be occurring in a recent report describing the chemistry of WSe<sub>2</sub> surfaces, in which improved WSe<sub>2</sub>/Au interface behavior was observed after electrochemical cycling of the WSe<sub>2</sub> anode in an aqueous I<sup>-</sup>/I<sub>3</sub><sup>-</sup> electrolyte.<sup>10</sup> Additionally, photowashing procedures have been recently advanced as a method for decreasing the sur-

face recombination velocity of GaAs interfaces,<sup>11</sup> and suitable control over the electric potential and the chemical constituents of the GaAs/liquid interface might yield additional control and reproducibility for this passivation process. Clearly, photoelectrochemical processing of semiconductor surfaces can have beneficial effects that are not attainable through conventional thermal processing techniques, and other applications of these methods are being explored at present.

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