# Ideal Schottky Diodes on Passivated Silicon

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Because of the complicated electronic and metallurgical properties of the metal-semiconductor interface, there is much controversy about the theoretical interpretation of experimental results on Schottky barrier heights. We present a new approach of barrier height measurements on a prototypical clean, abrupt and noninteracting system consisting of mercury contacts to hydrogen-passivated silicon surfaces. The resulting barrier to *p*-silicon is 0.9 V, totally at variance with all results presented for silicon Schottky barriers fabricated by standard metal deposition techniques. We believe this to be the first report in the limit of noninteracting metal contacts to silicon.

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The study of the band lineup between a metal and a semiconductor in intimate contact (Schottky barrier) has led to much controversy concerning the theoretical interpretation of experimental results. Current theoretical models of the band lineup can be divided into two groups. One group of theories proposes that the experimental results are intrinsic to the perfect interface [1]. According to this model the band lineup is determined by the neutrality level at which the Fermi level will normally pin. This opinion currently dominates the physics literature, despite questions as to the universality of the model. The other group of theories postulates an extrinsic effect, typically involving a metallurgical interaction between the metal and the semiconductor, but differing in such details as to the physical origin of this extrinsic effect [2,3]. For example, the two dominant extrinsic models for Schottky barriers both on silicon and on compound semiconductors speculate that the interaction results either in detect formation in the semiconductor material or in an interfacial layer made up of a metallic alloy or mixture of phases. The former model leads to deep levels in the semiconductor, hence changing the band-bending charge distribution within the semiconductor [2], whereas the latter leads to a change in the boundary conditions between the metal and the semiconductor in a simple model of the interface [3].

Any experimental attempt to distinguish between intrinsic and extrinsic models of the band lineup must in some fashion modify or eliminate the assumed extrinsic mechanisms. Such mechanisms usually invoke thermally driven or adsorption driven processes. Studies of interface formation at low temperatures have led to the observation of some differences in band alignments [4], but many of these differences are minor and obscured by experimental artifacts such as the photovoltage effects [5] in the photoemission techniques typically used in these studies. Clearly, a different method of investigation is needed on ideal, noninteractive metal-semiconductor interfaces to investigate the band lineup in Schottky barriers.

We report here a room-temperature approach which circumvents the possibility of heat of nucleation or adsorption to drive an interaction between the metal and the semiconductor. We achieve this by exploiting chemical passivation of silicon by a specific form of HF cleaning to attain a clean, stable silicon surface [6], followed by contacting this surface with a liquid metal probe [7]. In our case the metal is Hg, and the probe area is well defined by lithographic techniques. Recent reports establish that the passivated surface prepared by HF containing etchants is simply the outermost silicon layer terminated by hydrogen bonds [8,9]. Surface studies demonstrate that the hydrogenated layer is only a single monolayer [10], so we can expect an intimate contact between the metal and the semiconductor. Almost all metals react with silicon at some temperature forming a wide variety of silicides or alloys. Such reactions can be initiated even during room-temperature deposition of the metals and extend generally over at least a few monolayers [11]. In contrast, mercury, in equilibrium, will be completely inert on silicon surfaces [12]. Through its use as contacting metal we are not condensing a vapor, and hence need not consider heat of condensation, adsorption, or nucleation which may drive a nonequilibrium interaction between the contacting metal and the semiconductor. We shall demonstrate that this prototypical clean, abrupt, and noninteracting system provides band lineups that are incompatible with those expected from intrinsic models, and at variance with those observed in Schottky barriers formed by standard metal deposition techniques.

The substrates used for the fabrication of the Schottky diodes were epitaxial silicon wafers of (111) orientation. The high-resistivity epitaxial layer was 2 $\mu$m thick and doped with $2\times10^{15}$ B/cm$^3$, and the low-resistivity substrate was doped with $1\times10^{19}$ B/cm$^3$. An Ohmic contact was formed on the back side of the wafer by implanting 40 keV B to a dose of $5\times10^{15}$ cm$^{-2}$. A thin thermal oxide of 200 Å was first grown at 900 °C, followed by the deposition of a 3200-Å-thick low-temperature chemical vapor oxide at 420 °C. Subsequently, the oxide was densified at 800 °C for 30 min. These thermal treatments activated the previously implanted B. Redistribution of the dopants in the substrate and the epilayer was prevented by the use of low-temperature processes.

Circular windows of 500 and 1000 $\mu$m diameter were opened on the front side of the wafers and the oxide layer on the back side was completely removed by using standard lithography techniques. The back side of the wafers was then metallized with a bilayer of Ti and Au and annealed at 325 °C for 15 min in Ar environment. Then the wafers were cleaved into smaller samples with eight to sixteen diodes. These were subject to an RCA [13] clean. Immediately before applying the Hg contacts the samples were dipped into 10:1 diluted HF, rinsed in deionized water and blown dry with nitrogen. Small drops of Hg were then deposited over the contact openings with a syringe.

A Keithley model 230 programmable voltage source and a Keithley model 617 digital electrometer were used to record the *I-V* characteristic of the Schottky diodes. All *I-V* measurements were automated with a personal computer (IBM PC AT). Several current measurements were taken for each voltage step to improve the signal-to-noise ratio in the very low-current regime. The sample temperature was measured with a platinum resistance thermometer mounted in the solid metal holder of the sample tester. All measurements were performed in a dry nitrogen environment and the *I-V* data were taken in the dark.

The forward characteristic of a Hg/Si(111) Schottky diode with a diameter of 1000 $\mu$m is shown in Fig. 1. The silicon was etched in 10:1 diluted HF for 30 s and rinsed in deionized water for 30 s before the mercury contact was applied. The *I-V* characteristic is linear over 7 orders of magnitude in the semilogarithmic plot of Fig. 1. This is quite remarkable for a metal on *p*-type Si. At high forward bias the *I-V* characteristic deviates from a straight line due to the series resistance of the diode associated with the substrate, the back contact, and the external electrical connections. A fit of the thermionic-emission equation [14] to the data using a Richardson constant of $A^* = 32\ \mathrm{A\,cm^{-2}\,K^{-2}}$ yields a barrier height of $\phi_{bp} = 0.924$ V, an ideality factor of 1.019, and a series resistance of 7.45 $\Omega$. The departure of the ideality factor from the ideal value of 1.0 is due in large part to the image force effect. It causes a lowering of the barrier height by $\Delta\phi_{bi} = 0.013$ V and results in an ideality factor of $n = 1.010$. Another contribution to the nonideality stems from carrier recombination in the depletion region of the diode. Generally, it is the cause for higher ideality factors observed with a number of diodes. This will be discussed with the reverse characteristic of the diode. We do not correct for image force lowering in the measurements of the barrier height. The low series resistance clearly points out the advantage of using an epitaxial structure for the Si substrate and a good Ohmic back contact. We were unable to measure a rectifying characteristic of diodes prepared on *n*-type Si even at 200 K. This confirms the high barrier on *p*-type Si we observe.

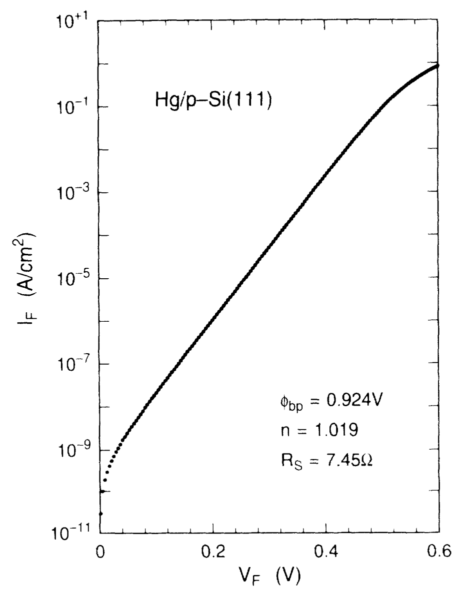


FIG. 1. Forward *I-V* characteristic at 295 K of a Hg/Si(111) Schottky diode with a diameter of 1000 $\mu$m representing a barrier height of 0.924 V and an ideality factor of 1.019. The silicon surface was etched for 30 s in 10:1 diluted HF and rinsed for 30 s in deionized water.

A concern with Hg contacts to Si is the wetting of the metal. We have measured the barrier height, which depends on the contact area through the current density, on diodes of different diameters. For diodes with a 500 $\mu$m diameter we found less than 30-mV change in barrier height compared with the 1000-$\mu$m diodes. This indicates that for the large diodes wetting of the metal is not a problem. However, pronounced deviations were found for diodes of 250 $\mu$m and smaller diameters. For this reason we are only presenting results for the 1000-$\mu$m diodes in what follows.

The reverse characteristic of a Hg/Si(111) diode is shown in Fig. 2. Ideally, the reverse current should saturate according to the thermionic-emission theory [14]. In practice, however, this is never the case. Lack of saturation is partly due again to the imaging force effect which results in a voltage-dependent barrier height. In addition, a significant contribution comes from carrier recombination in the depletion layer. This effect is common in Schottky diodes [14,15]. Carrier recombination is expected in Schottky diodes with high barriers at low temperatures, and occurs at the periphery of the diodes [16]. It is more prominent at reverse bias because of the larger electrical fields involved in this mode. The reverse current in Fig. 2 can be well fitted with an equation that is composed of two terms, a thermionic-emission component and a recombination component [15]. The fit yields a barrier height of 0.912 V and a carrier lifetime of $5.3\times10^{-5}$ s. The latter value is in good agreement with the published lifetime of $(4.85\pm2.6)\times10^{-5}$ s for high-quality *p*-type layers in the doping range of $10^{14}$ to $10^{17}$

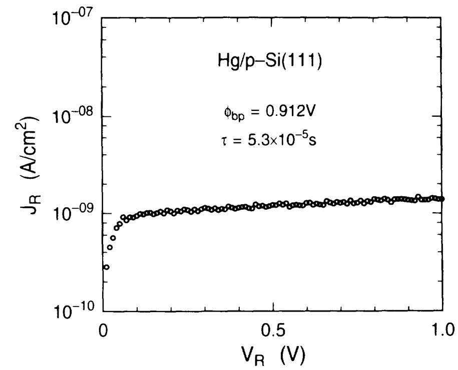


FIG. 2. Reverse *I-V* characteristic at 295 K of a Hg/Si(111) Schottky diode with a diameter of 1000 $\mu$m representing a barrier height of 0.912 V and a carrier lifetime of $5.3\times10^{-5}$ s. The silicon surface was etched for 30 s in 10:1 dilute HF and rinsed for 30 s in deionized water.

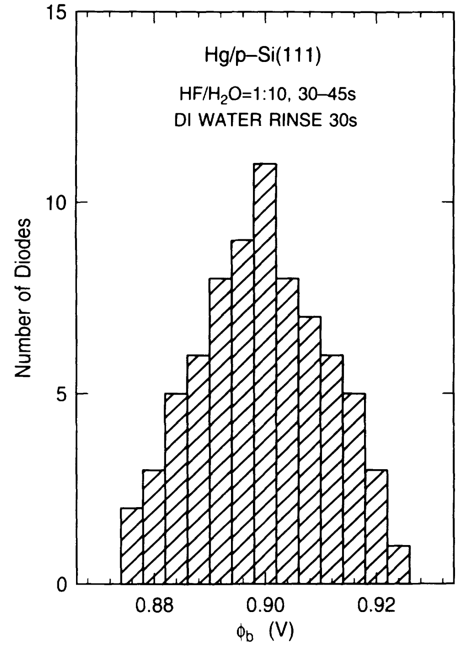


FIG. 3. Distribution of the barrier heights measured on 75 Hg/*p*-Si(111) Schottky diodes. The average effective barrier height is $0.902\pm0.012$ V.

cm$^{-3}$ (Ref. [17]).

These exceptional diodes with high barriers and good ideality are sensitive to the preparation of the silicon surface. It is known that etching solutions containing fluorine leave some fluorine residue at the silicon surface. In contrast to hydrogen, which is bonded to the silicon surface atoms, the fluorine is only physisorbed [6]. Thus, it can be easily removed by rinsing the silicon substrate in deionized water. Detailed studies have shown [9] that a short rinse removes most of the fluorine atoms from the etched silicon surface, whereas a prolonged rinse will cause the formation of O-H bonds at the silicon surface [18]. We have investigated in detail the effect of rinsing and found that the barrier height of Hg/Si diodes decreases at most by 40 mV for rinsing times between 30 s and 5 min. The best Schottky diodes were obtained for a rinsing time of 30 s. We investigated 75 Schottky diodes on a Si(111) surface which was etched in 10:1 diluted HF for 30 to 45 s and rinsed in deionized water for 30 s. The distribution of the measured barrier heights is shown in the histogram of Fig. 3. We find an average effective barrier height of $0.902\pm0.012$ V. The statistical analysis of the ideality factor yields an average value of $1.055\pm0.024$. The small scattering of the barrier height and the low ideality factor clearly point out the high quality of the Hg/Si(111) Schottky diodes. They also show that the current transport in these diodes is well described by the thermionic-emission theory.

The barrier height of 0.902 V for Hg on passivated Si(111) is the highest barrier height ever reported of any metal on *p*-type silicon. Most Schottky barrier heights published to date lie in the lower half of the band gap on *p*-type silicon. The few exceptions involve highly electronegative metals such as rare earths [19]. Even a recent photoemission study [20] of evaporated Hg on ultrahigh vacuum cleaned silicon puts the barrier height in the lower part of the band gap. This is not surprising; condensation from a hot vapor to a room-temperature substrate is not an equilibrium process and the silicon surface was not hydrogen passivated in that experiment. We are thus confident that the above barrier height is the result of an abrupt and noninteractive interface between Hg and passivated Si. At this point it is important to emphasize that the mercury is in intimate contact with the silicon. This follows directly from the high resolution infrared reflection spectroscopy studies performed at Bell Labs [8] and Fujitsu [9] on hydrogen passivated silicon surfaces which establish that the passivation consists of a single monolayer of silicon hydrides. Also, from these studies it follows that an interfacial oxide layer is absent. We confirm this by our measurement of the barrier height of Hg on a silicon surface covered with a $14.5\pm1.5$-Å-thick chemical oxide. The diodes with a thin interfacial oxide layer behave electrically like Schottky barriers, albeit with a smaller barrier height that is closer to that normally observed. In this case an average value of $0.814\pm0.015$ V is found which is about 90 mV below the value for the oxide-free interface. The resulting difference in barrier height of 90 mV for these two cases is significant.

In the simple model of the metal-semiconductor interface described by Schottky [21], the barrier height of a metal on *p*-type silicon is given by $\phi_{bp}=(E_g/q)+X-\Phi_m$, where $E_g$ is the band gap of the semiconductor, $q$ is the electron charge, $X$ is the electron affinity of the semiconductor, and $\Phi_m$ is the metal work function. With $E_g=1.12$ eV at 300 K, $X=4.2$ V for Si [22] and $\Phi_m=4.49$ V for Hg [23] we find $\phi_{bp}=0.83$ V. Although the barrier height of Hg on the thin oxide covered silicon surface is in better agreement with the Schottky picture, the value for the passivated silicon surface is also within the $\approx 0.1$ V accuracy range expected of this model. In the extreme of thick oxide layers the flatband voltage is directly proportional to the metal-semiconductor work function difference as is well known from metal-oxide-semiconductor (MOS) structures. In the other extreme of the absence of an interfacial oxide layer the barrier height is directly dependent on the electronic properties of the intimate metal-semiconductor interface. Our results probe these limits differently than have previous experiments.

The reduced dependence of the barrier height of metal-semiconductor interfaces on metal work function is usually ascribed to pinning of the Fermi level by interface states. Intrinsic [1] as well as extrinsic [2,3] origins have been proposed for these states. We believe that through the passivation of the silicon surface we have eliminated the extrinsic effects. Our observed high value of the Schottky barrier for Hg compared to other metals on $p$-Si diodes indicates a strong difference between the present and all previous studies, and that this difference is related to the completely noninteracting technique used to prepare the diodes. Two possibilities are evident: (1) All previous results are extrinsic, due to the metallurgical interactions previously discussed [2,3] and difficult to rule out at the small level of interaction required to alter the results from an intrinsic level, or (2) we have changed the properties of the silicon surface layer. Possible changes include removal of surface states from the band gap, altered surface dipole induced by hydrogen chemisorption, or different dielectric constant of the surface layer [24]. All these changes can affect the intrinsic position of the Fermi level at the interface. Since the screening length is on the order of the bond length, one monolayer of silicon hydride is sufficient to control the position of the Fermi level [25].

For either explanation to be valid we have have no interaction between the metal and the silicon. This supports the exclusion of extrinsic interactions in the present experiment.

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