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# Pb/Si(111)1×1–H SCHOTTKY BARRIER HEIGHT

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We studied Schottky barrier height of lead on n– and p–type ideally terminated Si(111)$1 \times 1$–H unreconstructed surface by electrical measurements and X-ray photoelectron spectroscopy (XPS). The hydrogenation of the Si(111) surface was done by means of wet etching in HF and $NH_4F$. The deposition of Pb was made under ultrahigh vacuum conditions. There are differences between the barrier heights from the $I - V$ and from the XPS measurements. The reasons seem to be a bad wettability of Pb to Si(111)$1 \times 1$–H and a possible surface reconstruction of Si under the thicker metal film.

## 1. Introduction

The physical mechanism responsible for the formation of metal – semiconductor barrier is not understood yet. Several hypotheses were suggested since Schottky formulated his model based on the difference between the metal work function and electron affinity of the semiconductor [1], e.g., the model of Bardeen [2] with the Fermi level pinning at the interface due to the interface states in the semiconductor band gap.

Ideally terminated $1 \times 1$ surface of Si(111) – truncated bulk, obtained by saturation of dangling bonds by hydrogen, is a subject of intensive study [3 - 5]. This type of surface is commonly prepared by aqueous HF and/or $NH_4F$ etching. Such a surface is attractive both from a technological and a surface science point of view because of extremly high flatness and bulk–like termination.

Tung has shown in his pioneering work [6] that the Schottky barrier height (SBH) depends on an interface crystallography. Recently, Hestlinga et al. [7] reported the same effect for the barrier height of Pb/Si(111) diodes which depended on the type of surface reconstruction. They ascertained that the two structures, which differ only in the arrangement of the first layer of Pb and Si atoms at the interface, have different SBH. The Pb/Si(111)$7 \times 7$ structure has SBH of 0.70 V and the Pb/Si(111)$\sqrt{3} \times \sqrt{3}R30^\circ$ has SBH of 0.93 V.

Lead is known to create unreactive interface with Si, and that is why it is convenient metal for the study of metal – silicon interface. Mutual solubilities between Pb and Si are expected to be negligible [8]. For these reasons it is interesting to explore the behaviour of the Schottky contact made from the ideally terminated silicon surface with the nonreactive metal, Pb. The fulfilment of Schottky's limit can be expected.

SBH's are experimentally measured by several techniques. The most obvious methods for the structures with relatively thick metal layers (several tens or hundreds of nm) are $I - V$ and $C - V$ measurements. In the X-ray photoelectron spectroscopy (XPS) method, SBH can be determined from the energy shift of core–level spectra of semiconductor atoms after the metal deposition.

There are almost always discrepancies between the values of SBH measured on the same structures with different techniques. One of the reasons for the differences is, for example, interface inhomogeneities which differently influence different kinds of measurements.

## 2. Experimental

For the preparation of Schottky diodes we used moderately doped Si(111) substrates. n–type phosphorus doped Si had the resistivity $\rho = 100\ \Omega$cm (dopant concentration $\approx 6 \times 10^{13}$ cm$^{-3}$), p–type Si was boron doped with the resistivity $\approx 10\ \Omega$cm (dopant concentration $\approx 1 \times 10^{15}$ cm$^{-3}$). The wafers were first thermally oxidized at 1050 °C with a 15 min post annealing at the same temperature in an inert gas. The substrates were then etched in HF and the last step was 2 min etching in $NH_4F$ in order to leave only SiH on the sample surface. Immediately after etching, the samples were carefully introduced into a vacuum chamber pumped only by a turbomolecular pump (without the ion pump) in order to avoid splitting of hydrocarbons. The evaporation of lead from Knudsen cell was done under ultrahigh vacuum conditions. The typical rate of evaporation was $10^{-3}$ nm/s. Lead was evaporated stepwise from submonolayer coverages up to the thickness of 120 nm. Circular diodes with a diameter of 0.9 mm and 0.5 × 0.5 mm square diodes were prepared. To make an ohmic contact, a Ga contact was made on the abraded back side of the p–type wafer and for the n-type Si, a 20 nm layer of Cr was evaporated onto the wafer before Ga was applied [9]. The diode parameters were derived from the $I - V$ curves by a standard fitting procedure.

## *3. Results*

The growth mode of lead was controlled by Pb 5d and Si 2p core–level intensity development by XPS measurement during the layer growth. The dependence of thickness of the line intensities showed Stranski–Krastanov layer–plus–islands growth mode (Fig. 1). Si(111)1×1-H surface structure was observed by a low-energy electron diffraction (LEED) immediately after the insertion of the samples into the chamber and after each evaporation step, and remained visible up to several monolayers of lead evaporation. The diffuse hexagonal spots were visible even after the deposition of 120 nm of lead.

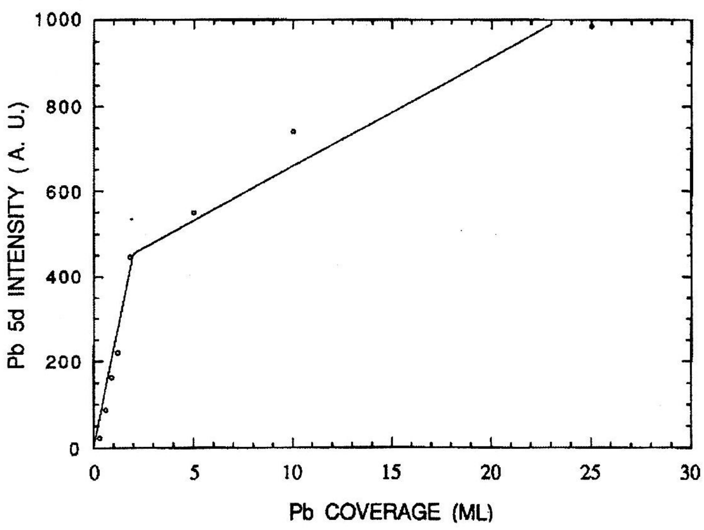
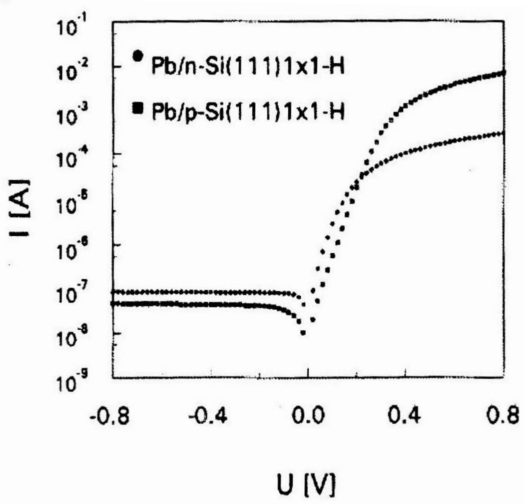



*Fig. 1 Evolution of the intensity of* Pb 5d *core level line during the deposition of* Pb *onto the* Si*(111)*1 × 1–H *surface.*

The $I-V$ characteristic of the n– and p–type diodes are shown in Fig. 2. Despite very careful preparation techniques, the dispersion of the barrier heights of n–type diodes from one wafer was relatively high. This indicates that the interface is not homogeneous. The mean value of the barrier height from ten structures of the same wafer was 0.71 V. The best measured ideality coefficient was 1.05.

The average barrier height of 20 structures on p-type Si is 0.72 V. The dispersion of the barrier heights is lower than for the n–type structures. The best measured ideality coefficient was 1.14. The barrier height distribution is shown in Fig. 3.

The reverse current saturates in both cases, and there is no remarkable excess current due to the leakage or generation-recombination conduction mechanisms.



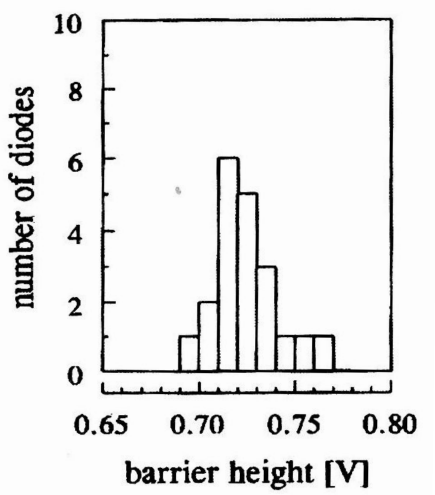




*Fig. 2. Typical $I - V$ curves of* Pb/n–Si*(111)*1×1–H *and* Pb/p-Si*(111)*1 × 1–H *diodes. The contact area was* $6.4 \times 10^{-7}$ m$^2$.

*Fig. 3. Statistical distribution of the SBH's* Pb/p–Si*(111)* 1 × 1–H *diodes (right).*

In the initial stages of the Pb film growth, the interface was also studied by high resolution synchrotron radiation photoemission spectroscopy. The spectra were measured by the same equipment as used by Hricovini et al. [10] to study Si(111)1 × 1–H surface.

## 4. *Discussion*

The Si 2p XPS spectra with 2.5 ML's deposition were remarkably similar to the unexposed ones; only the intensity was reduced. The persistence of all original components of the spectra with the same weights and just slightly increased Gaussian widths was the proof that the H layer remained practically unaffected at the interface. The issue is discussed in more detail in Ref. 8. The position of the Fermi level ($E_F$) at the Si surface, immediately after the insertion into to chamber, was exactly the same as in the bulk, i.e. the bands were flat and the $E_F$ is unpinned. In principle, one has to consider also an effect of surface photovoltage (SPV), which could influence the XPS results mainly for semiconductors with reasonably large band gaps or at low temperatures. The SPV supresses band bending and has opposite sign for n– and p–type semiconductors. Indirect proof that there was no influence of SPV is band bending in the same direction for n– and p–type Si after starting the Pb deposition.

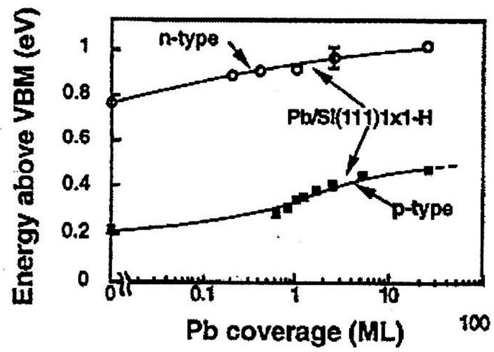



*Fig. 4 Surface $E_F$ position as a function of* Pb *deposition. The position for* Si*(111)*1 $\times$ 1–H *corresponds to the flat band conditions.*

The development of the $E_F$ position with Pb layer thickness for n– and p–type structure is given in Fig. 4. For both n- and p-type Si, $E_F$ moves upward in the bandgap; at 25 ML's coverage it is 0.45 eV above the valence band maximum (VBM) of p–Si structure and 0.07 eV below the conduction band minimum (CBM) of n–Si.

From the inertness of the Pb/Si(111)1$\times$1–H, one could expect that the structure would behave closely in accord with the Schottky–Mott theory and the barrier height would be determined by the difference between the work function ($W_F$) of Pb and the electron affinity ($\chi$) of Si. According to the published values of $W_F$ of Pb (3.9 eV) [11] and $\chi$(3.83 eV) [8], the SBH for n–type Si should be $\approx$ 0.07 V for n–type Si and 1.05 V for p–type Si. With this assumption only the position of the $E_F$ for n–type Si is consistent. The SBH for p–type Si obtained from XPS is $\approx$ 0.45 V.

Downward band bending for n–type Si structures anticipates ohmic electrical behaviour for Pb/n–Si(111)1 $\times$ 1–H thick diodes. However, the electrical measurements show that it is not true. The discrepancy was found also between the XPS and electrical measurement concerning the SBH's on p-type Si which were 0.45 V and 0.72 V, respectively. The difference between SBH's from XPS and electrical measurements of similar magnitude has been previously observed for Pb/Si(111)7 $\times$ 7 structure (12). From Fig. 4 it is seen that the final position of $E_F$ was, probably, not established at least for p–Si. As we have already pointed out, the clear 1 $\times$ 1 structure was visible in LEED also after 20 ML's of Pb deposition. It is the consequence of layer–by–islands growth. Even at a Pb layer thickness of 120 nm, the observation by scanning electron microscopy (not shown) revealed that the coalescence of the islands has started, the channels were created, but still the film was not continuous. Pb does not wet the hydrogen terminated Si surface very well and tends to minimize the contact area with the Si similar to findings reported in Ref. 13. The same effect is supposed to hamper the coalescence of the islands. The Stranski–Krastanov growth mode may also cause differences in the surface $E_F$ position under the islands and the rest of the surface because the $E_F$ shift is not finished when the islands start to grow.

The SBH's for n– and p–type diodes do not sum up to the bandgap. The reason for that, at least in part, is the difference between the actual Schottky diode area and the macroscopically measured one because of the bad wettability. The calculated SBH's are, therefore, higher than the real ones. However, this fact alone cannot change the apparent barrier height to the extent necessary for explaining the difference. It is an inherent feature of an exponential type of $I - V$ characteristics that it is only very slightly sensitive to the error made in the contact area determination [14].

The first electrical measurements of the barrier height of the metal/hydrogen terminated Si(111) were published by Wittmer and Freeouf. They have studied mercury contact on the Si(111) at the atmospheric ambient pressure. The rectifying characteristics were obtained only for p–type Si and the SBH was 0.90 V for HF treated [15] and 0.85 V for structures with $NH_4F$ treatment as a last step [16]. Because the SBH was size dependent, authors supposed that there were problems with wettability of mercury. They have ascertained a 30 mV SBH difference at 295 K when reducing the diameter of the diode from 1000 $\mu$m to 500 $\mu$m. For further contact area reduction even greater differences were reported.

Many questions remain open. Different SBH's were measured by $I-V$ technique and XPS measurements. For Pb/n-Si(111)1 × 1–H structure XPS shows Schottky–Mott behaviour. It was shown that surface position of $E_F$ can move in n-Si(111) from 0.19 eV above VBM for $\sqrt{3} \times \sqrt{3}$ R30° surface structure [7] to 0.07 eV below CBM for 1×1 reconstruction, i.e. a 0.86 eV shift throughout the band gap. However, final $E_F$ position was probably not established for p–type Si even after the 25 ML's Pb deposition.

## 5. *Conclusion*

Electrical and XPS measurements of barrier heights on Pb Schottky diodes made both on n– and p–type hydrogen–terminated Si(111) have been reported. For the difference between the sum of n– and p–type barrier heights from electrical measurements and the Si band gap is, at least partially, responsible different actual and apparent contact area. Possible interface reconstruction under the thicker metal film, which is difficult to observe, might have caused the non-establishment of the final common position of $E_F$ at the surface by XPS.

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## VISINA SCHOTTKYJEVE BARIJERE Pb/Si(111)1×1–H

Električnim mjerenjima i rendgenskom fotoelektronskom spektroskopijom (XPS) proučavana je visina Schottkyjeve barijere olova na n– i p– idealno završenoj nerekonstruiranoj površini Si(111)1×1–H. Hidrogenizacija Si(111) površine načinjena je jetkanjem u vodenoj otopini HF i $NH_4F$. Olovo je napareno u ultravisokom vakuumu. Opažena je neusklađenost rezultata za visinu barijere $I-V$ i XPS mjerenjima, što se tumači lošom močivošću Pb na Si(111)1 × 1–H i mogućom obnovom površine Si pod debljim slojem Pb.