

Organic Modified Mercury-Silicon Junctions: Device Performance and Electron Transport

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Metal-semiconductor (M-S) junctions have been widely used in creating ohmic contacts, Schottky diodes, and metal-insulator-semiconductor field-effect transistors. The fabrication and testing of M-S junctions directly affect the process, characteristics, and performance of these important elements in electronic devices.¹ With the emergence of molecular modification and self-assembly techniques, research activities have been bolstered with the aim of obtaining a full understanding of metal-molecule-semiconductor interfaces. Silicon is the most popular material in the fabrication of electronic devices; it is of great importance from both fundamental and application perspectives to control the chemical and physical properties of the interfaces between silicon and metals at the molecular level. Studies of the organic modification of silicon has been of increasing interest as it provides a promising approach to improve its stability as an electrode, to achieve ideal surface passivation, and to develop silicon based molecular electronics.²

As our first set of experiments, we have explored the use of alkyl monolayers formed on oxide-free silicon to change the interfacial nature of metal-semiconductor junctions, *i.e.*, effectively passivating the silicon surfaces and molecularly tuning the effective barrier height of the diode junctions. In particular, we use a series of Grignard reagents ($n\text{-C}_n\text{H}_{2n+1}\text{MgBr}$, $n = 6, 8, 10$, and 12) to form robust and uniform alkyl monolayers on hydrogen terminated n -type silicon (H-Si). For a direct Hg|H-Si junction, the measured current density is perfectly linear with respect to the bias voltage, *i.e.*, exhibits the typical ohmic contact characteristics. In contrast, the molecularly modified junctions show clear rectifying behavior, *i.e.*, the currents under forward bias are significantly higher than those under reversed bias. More interestingly, for the series of Hg|C_nH_{2n+1}-Si ($n = 6, 8, 10$, and 12) junctions, the longer the alkyl chain, the lower the current density.

The comparison between the current-voltage curves shows qualitatively that alkyl monolayers imposed at the interfaces drastically change the device performance of the mercury-silicon junctions. To understand this, we calculated the junction's effective barrier height and the ideality factor based on the Schottky thermionic emission model,¹ with an empirical consideration of the insulating organic film imposed at metal-semiconductor interfaces. Two conclusions are instant from the calculations: first, the ideality factors show no clear dependence on the alkyl chain length within the experimental uncertainties, and they are substantially smaller (close to the unity) compared to that of a direct Hg|H-Si junction (2.76 ± 0.05). Second, the effective barrier heights are significantly higher than that of a Hg|H-Si junction (0.46 ± 0.05 eV). As predicted, the longer the alkyl chain, the higher the effective barrier height. A linear fit to the dependence of the effective barrier height on the monolayer thickness, yields the electron tunneling constant, $\beta = 0.63 \pm 0.10 / \text{CH}_2$ in the mercury-monolayer-silicon junctions, which seemingly deviates

from the value reported for alkyl monolayers on silicon prepared and examined differently.³

To further understand the electrical properties at passivated metal-semiconductor interfaces, two types of mercury-insulator-silicon (n -type) junctions, *i.e.*, Hg | C₁₀H₂₁-Si and Hg | SiO₂-Si, were compared in detail based on their current-voltage and capacitance-voltage characteristics. Both of them exhibit near-ideal rectifying behavior with excellent saturation current at reverse bias, which is in contrast to the ohmic behavior of an unmodified mercury-silicon junction. Further theoretical evaluations confirmed that junctions modified with n -decyl monolayers possess higher effective barrier height, lower ideality factor (*i.e.*, closer to the unity), and better reproducibility compared to those passivated with native silicon oxide thin films. In addition, the dopant density and build-in potential, extracted from capacitance-voltage measurements of the organic modified mercury-silicon junctions, revealed that alkyl monolayer derivatization does not alter the intrinsic properties of the silicon substrate, and the surface state density at the alkyl monolayer | silicon interface is slightly lower than that of the silicon oxide | silicon interface.

Our investigations were also extended to questions related to the semiconductor processing and quality control. As one of the critical problems, contamination of semiconductor surfaces by organic species significantly deteriorates the quality and performance of ever-smaller semiconductor devices in ultra-large-scale integrated circuits. The adsorption behavior and impact of organic contaminants on silicon wafers upon storage and processing have been investigated indirectly by using spectroscopy techniques. Our solid-state electrical measurements showed that the electrical properties of H-Si are significantly influenced by the surface contamination upon exposure to air under ambient conditions. The current - voltage curves display a unique transition from ohmic to diode characteristics when the H-Si surfaces are exposed to air before the assembly of mercury-silicon junctions. In addition, the time-dependent results indicate that organic contamination dominates the initial stage, and slow oxidation is involved in the long-term process for the overall degradation of the electrical performance.

In summary, we have systemically studied the electrical properties of organic modified mercury-silicon junctions, *i.e.*, explored the use of alkyl monolayers to change the interfacial nature of metal-semiconductor junctions, compared the device performance of alkyl monolayers protected mercury-silicon junctions and those passivated with native oxide thin films, and provided direct information of the electrical degradation of silicon wafers upon exposure to air under ambient conditions. Several aspects of our approach deserve further investigation including the detailed understanding of the electron transport mechanism and the introduction of different molecular modification routes. Nevertheless, this work, essentially, brings organic modification at the molecular level one step closer towards the next generation of electronic devices.

References

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