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Short communication

Effect of hydrogen on interface of metal–semiconductor Schottky diode

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ABSTRACT

The effect of hydrogen on p-type Si/Mn and Si/Co Schottky diode has been investigated in present studies. The variations of *I–V* characteristics suggested that the rectifying act of these diodes change with variation of hydrogen pressure, which is due to the diffusion of hydrogen through the Mn and Co metal films up to Si surface or a creation of surface states at the interface. It is also observed that the effect of hydrogen found to be reverse in order for forward as well as reverse direction of current in Mn and Co deposited films on Si substrate, corresponding to anionic and protonic model of hydrogen interaction with metals. One can say that hydrogen plays an amphoteric role to neutralize either donors or acceptors level in semiconductors and metals. The Raman spectra of Si/Mn and Si/Co are taken and stoke lines link with the presence of hydrogen is observed. In this paper, we are presenting the role of hydrogen pressure on *I–V* characteristics at the interface of metal–semiconductor structure.

1. Introduction

The properties of metal–semiconductor contacts have been studied for many years, but the physical properties behind the metal–semiconductor junction, the lack of their reproducibility and the role of hydrogen are still unclear. Recently, the use of hydrogen has gained considerable attention in industry as fuel cell and fueled motor vehicles. Due to safety reasons, the monitoring of hydrogen has become an important issue for scientists. The detection of hydrogen gas by Schottky diodes for different materials was observed by many authors [1–4]. The metal silicon contacts perform certain interest in such research because they are the cheapest among semiconductor sensors. The hydrogen is chemisorbed in the interfacial zone and modified electrical charges [5].

The Pd/InGaP metal–semiconductor Schottky diode was reported by Lin et al. [6] for hydrogen sensors. They suggested that variation of Schottky barrier height increases with the increase of the operating temperature and hydrogen concentration. Poteat et al. [7] observed hydrogen sensitivity in Pd–GaAs and suggested that diffusion of hydrogen through the Pd metal and creation of surface state at the interface was responsible for sensitivity. It was also suggested by authors [8,9] that the breakdown behavior has been due to the large fringing fields (the electric fields produced by scattered electrons) developed at the sharp edges of the porous surface, which can be orders of magnitude larger than that of a smooth area Schottky diode under the same condition. Hence, metal–semiconductor junction is a novel hydrogen sensor, which can detect hydrogen at room temperature. When hydrogen is introduced, the ambient gas inside the pores is replaced and the breakdown voltage increases. The low temperature operation of these detectors as well as their fast response and recovery time could be of great practical interest. The electrical, optical and *I–V* characteristic studies of Al/Sb and In/Sb

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bilayer structures carried out by Singh et al. [10,11] was to observe the effect of annealing temperature on mixing of the interface, and suggested that variation is found to be in optical properties at the interface. The effect of hydrogen pressure on FeTi and FeTi–Mn observed by Singh et al. [12] and suggested that hydrogen takes electron from inter-metallic structure. The effect of annealing temperature on electrical characteristics of Co/p-type Si Schottky barrier diodes was observed by Gular et al. [13] and suggested that barrier height increased with annealing temperature due to the removal of passivation effect of the native oxide layer and reactivates the surface defects. The decrease of barrier height of Pt/GaN diode with hydrogenation was measured in *I–V* characteristics by Schalwing et al. [14] and suggested that current increased in reverse direction due to the reduction of barrier heights. They had also used elastic recoil detection (EDR) to determine an accumulation of hydrogen on the Pt surface as well as at the interface of Pt/GaN and reveled preferential hydrogen adsorption sites on the surface and at interface. Ruths et al. [15] used Pd/Si Schottky barrier diode for hydrogen detection and suggested two hypothetic mechanisms: (1) hydrogen atoms were polarized and dipolar layer is raised; (2) the excess charge state at the interface were induced by hydrogen atoms. Hence, according to them, diode current increased due to the presence of hydrogen atoms at Schottky interfaces. The hydrogen sensing performance of electroless plated and thermal evaporated Pd/InP Schottky diodes observed by Chen and Chou [16] and suggested that current in the forward and reverse directions increased with increasing hydrogen concentration. The Raman study was carried out by Leitch et al. [17] for hydrogenation of crystalline silicon. They suggested that incorporation of hydrogen shows the characteristic peak at 2100 cm^{-1} and a broad peak also observed by Heyman et al. [18] at 2129 cm^{-1} to confirm the Si–H bonding. The annealing temperature effect on electrical characteristics of Co/p-type Si Schottky barrier diodes observed by Guler et al. [13], but no one observed the effect of hydrogen gas pressure on electrical characteristics of these diodes in our knowledge.

2. Experimental

Thin film of Mn (99.98%) and Co (99.998%) powder of Alfa Aesar (USA) is deposited on ptype boron doped silicon (1 0 0) using a thermal evaporation by hind high vacuum system at pressure 10^{-5} Torr, using tantalum boat. The thickness of Co and Mn deposited film is 100 nm measured by quartz crystal thickness monitor and confirm by ellipsometry measurements. The ohmic contact formed on these samples by silver paste in front of the metal film as well as on the Si substrate. Keithely-238 high current source measurement unit used to measure the *I–V*-characteristics and Raman spectra of annealed and hydrogenated Si/Mn and Si/Co samples are taken by a continuous wave-Green laser with a wavelength of 532 nm at room temperature by the help of R-3000 Raman system.

These samples are rapid thermal annealed to prepare diffuse interface junction and carried out the study of the *I–V* characteristic, The *I–V* measurement was performed thrice (1) immediately after deposition, (2) after rapid thermal annealing and (3) after hydrogenation with different pressures. The relative resistance and Raman spectra also recorded in order to see the effect of hydrogen gas pressure. The rapid thermal process carried out only for 2 min for making the Schottky junctions. The samples are kept inside quartz tube and rapidly annealed by using 500-Watt halogen lamp. Hydrogen gas is introduced in hydrogen gas chamber only 30 min for each hydrogen pressure cycles. After that relative resistance and the *I–V* characteristic are measured to see the effect of hydrogen gas pressure on electrical properties. The Raman spectroscopy is used to confirm the presence of hydrogen.

3. Result and discussion

3.1. As grown and rapid thermal annealed Si/Mn interface

The *I–V* characteristics of Si/Mn interface as deposited and rapid thermal annealed samples are shown in Figs. 1 and 2. The *I–V* characteristics of as deposited, without hydrogen, show the rectifier behavior having a low current in forward direction and higher current in the reverse direction. When pressure of hydrogen gas increases from 20 to 80 psi, the current in forward direction increases with hydrogen pressure continuously up to 40 psi, but after that current found to be decreasing on 60 psi (see in Fig. 1), it means this sensor can work up to the optimum pressure 60 psi. Basically, it has been commonly believed that adsorbed hydrogen atoms at the Schottky interface are responsible for the modulation of the *I–V* characteristics of Mn Schottky diodes. Owing to the specific perm-selectivity property of Mn, hydrogen molecules are firstly dissociatively adsorbed on the Mn surface and sequentially penetrate through the Mn film up to the Mn–Si interface. The increase in forward current is attributed with electron donation by hydrogen to the conduction band of deposited film and decrease in reverse direction due to accumulation of hydrogen.

In Fig. 2, drastic changes are found in *I–V* characteristics, it means after annealing as well as hydrogenation, the barrier height is much reduced. In the annealed samples, variation of current in reverse direction increase very fast and saturate as theoretical prediction for Schottky diodes. Hence, the effect of hydrogen in forward as well as reverse biased direction predominates due to large electrical

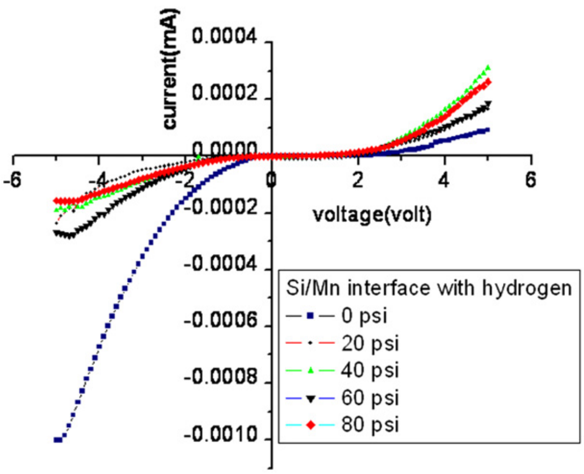

Fig. 1. *I–V* characteristics of Si/Mn interface as deposited at different hydrogen gas pressures.

polarization across the interface of *M–S* junction. The difference in *I–V* curves between as deposited and annealed is due to high sensitivity of hydrogen gas after annealing and passiveness, the defects especially under reverse bias condition. The junction exhibits a breakdown-type current voltage curve, whose breakdown voltage depends on the gas content inside the interface. The breakdown behavior has been attributed to the large fringing fields developed at the sharp edges of the interface due to the large accumulation of hydrogen, which can be an order of magnificence larger than that of a smooth area Schottky junction under the same condition. Similar results also observed by Ruths et al. [15] used Pd/Si Schottky barrier diode for hydrogen detection and suggested two hypothetic mechanisms (1) hydrogen atoms were polarized and give a raised dipolar layer; (2) the excess charge state at the interface was induced by hydrogen atoms. Hence, according to them diode current increased due to the presence of hydrogen atoms at Schottky interfaces. The increase behavior of current in forward and reverse directions, also observed by Chen and Chau [16], with an increase in hydrogen concentration well agrees with our result.

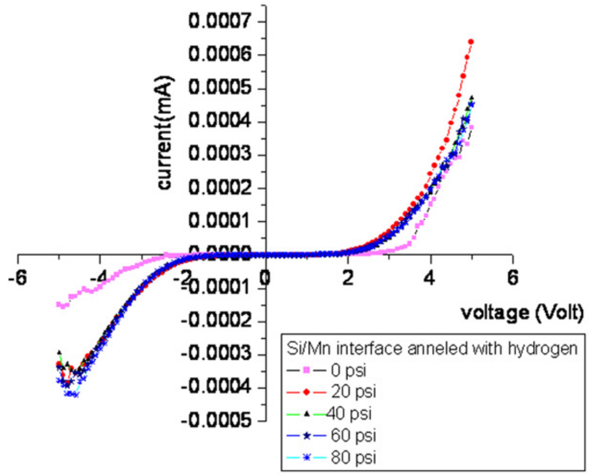

Fig. 2. *I–V* characteristics of Si/Mn annealed interface at different hydrogen gas pressures.

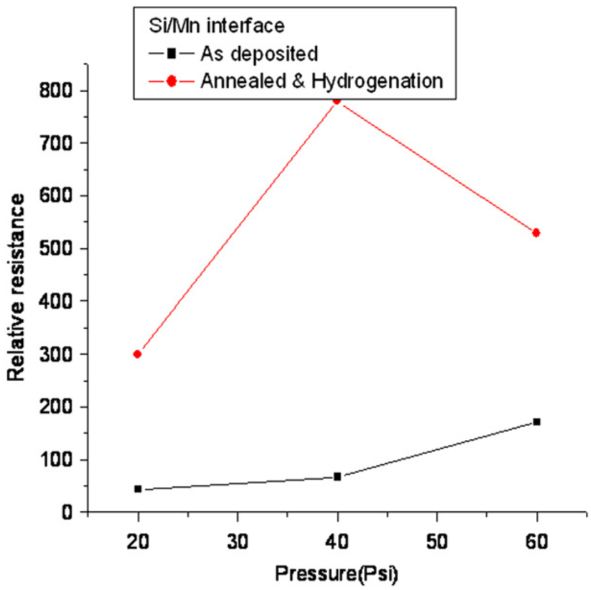

Fig. 3. Variation in relative resistance of as deposited and annelid Si/Mn interface with hydrogenation.

Fig. 3 shows the variation in relative resistance versus pressure of fully hydrogen-loaded samples both as deposited and rapid thermal annealed. Relative resistance is found to be very low in as deposited compared to annealed samples. This may be due to large absorption capacity of hydrogen by Mn thin films after surface activation due to annealing and accumulation of hydrogen at interface. It is noted by us that in annealed samples relative resistance increases linearly up pressure 40 psi, but further increase in pressure reduced the resistance, it again shows the large number of electron donated to metal–semiconductor junction by hydrogen atoms.

Fig. 4 shows the Raman spectra of Si/Mn samples. One can see that the intensity was increased with increasing pressure of hydrogen, which obviously shows the increase in the content of hydrogen in these samples. The Raman stoke peaks were observed at 1934, 2123.7 and 1922, 2142 cm^{-1} for 40 and 60 psi in hydrogenated samples, respectively. These peaks confirm the presence of hydrogen. Similar results were observed by Leitch et al. [17] in case of hydrogenation of crystalline silicon. They suggested that incorporation of hydrogen shows the characteristic peak at 2100 cm^{-1} and broad peak also observed by Heyman et al. [18] at 2129 cm^{-1} to confirm the Si–H bonding. Our results were slightly differing due to the large hydrogen absorption at the Si/Mn interface.

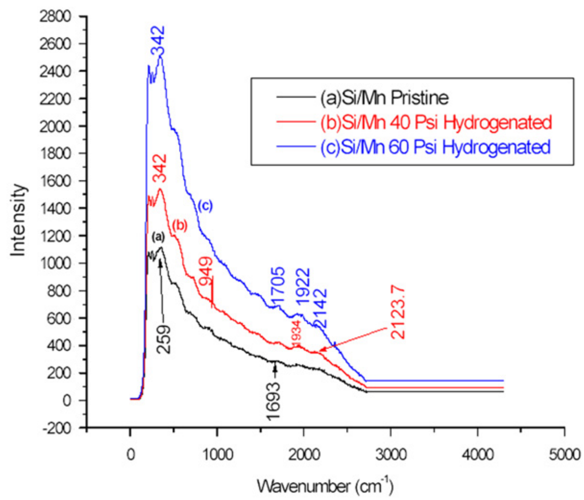

Fig. 4. Raman spectra of annealed Si/Mn interface.

3.2. As grown and rapid thermal annealed Si/Co interface

Fig. 5 shows the Si/Co Schottky diode interface as deposited, when hydrogen was introduced at different pressures (from 0 to 80 psi) then

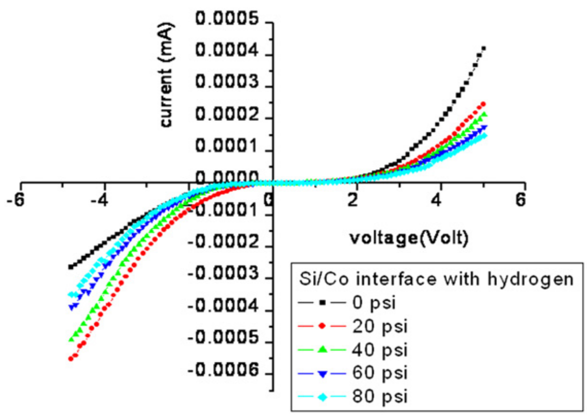

Fig. 5. *I–V* characteristics of Si/Co interface as deposited at different hydrogen gas pressures.

the *I–V*-curve found to change with hydrogen pressure. It suggests that hydrogen takes electrons from Co thin film and block the flow of charge carriers across the interface and decrease current in forward direction, but found to increase in reverse direction due to accumulation of hydrogen at interface and decreasing of barrier heights in reverse direction. The effect of annealing temperature on electrical characteristics of Co/p-type Si Schottky barrier diodes was also observed by Gular et al. [13] and suggested that barrier height increases with annealing temperature due to removal of passivation effect of the native oxide layer and reactivates the surface defects. We also observed decrease in current in forward direction it may be due to reactivation of defects, due to hydrogenation.

In Fig. 6, the *I–V* characteristic is found to be changed in both directions of current. It is also observed that increase in current in case of rapid thermal annealed samples compare with as deposited. Because of accumulation of charges at interface play an important role to decrease barrier heights, both forward and reverse currents increase with increasing hydrogen concentration caused by the decrease of barrier height, these results agree well with electrical polarization observed at interface [6]. Our results are also indicating that current increases five times rather than as deposited samples, compared to anneal samples, for the same bias after hydrogenation.

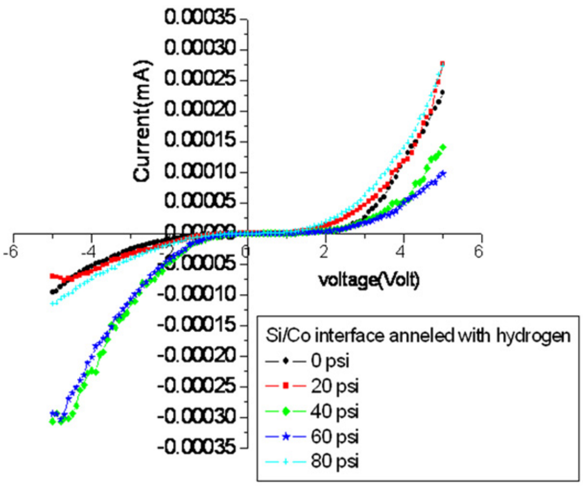

Fig. 6. *I–V* characteristics of Si/Co annealed interface at different hydrogen gas pressures.

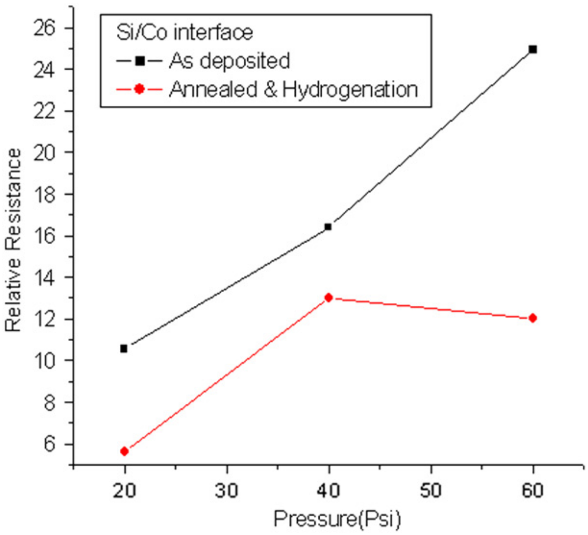

Fig. 7. Variation in relative resistance of as deposited and annealed Si/Co interface with hydrogenation.

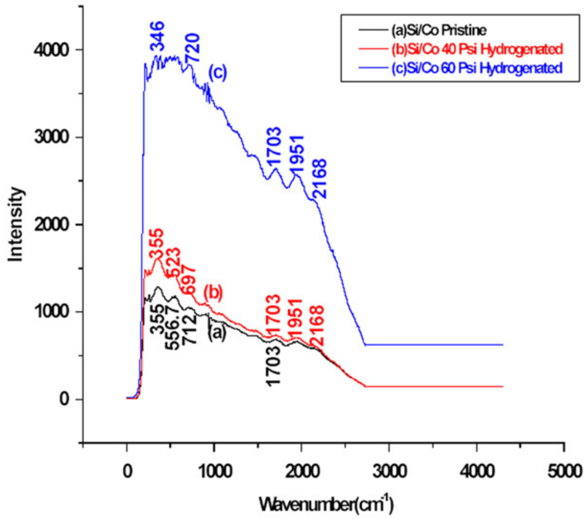

Fig. 8. Raman spectra of annealed Si/Co interface.

Fig. 7 shows the variation in relative resistance versus pressure of fully hydrogen-loaded samples, both as deposited and rapid thermal annealed samples. The relative resistance ratio found to decrease in annealed samples. It may be due to reduction of charge carriers during hydrogen absorption. It is also noted that it is the reverse effect compared to Si/Mn samples. The effect of hydrogen pressure on resistivity of FeTi and FeTi–Mn thin film observed by Singh et al. [12] and resistively found to increase with hydrogen absorption and supported the anionic model of hydrogen absorption in metallic thin films.

Fig. 8 shows the Raman spectra of Si/Co samples. We observed that the intensity is increased with increasing pressure of hydrogen, which confirms the increase in content of hydrogen in these samples. The Raman spectra stoke peaks are observed at 1951 and 2168 cm^{-1} for both 40 and 60 psi in hydrogenated samples. These peaks confirm the presence of hydrogen at interface. Similar results were observed by Heyman et al. [18] at 2129 cm^{-1} to confirm the Si–H bonding. Our results are slightly differing due to the hydrogen absorption at the interface of Si/Co.

4. Conclusion

1. The effect of hydrogen on *I–V* characteristics found to be reverse in Si/Mn and Si/Co systems because in case of Si/Mn hydrogen donates electrons to conduction band of metal as an anionic model and in case of Si/Co hydrogen takes electron from conduction band of metal as protonic model.
2. The variation of current in *I–V* characteristics curve with hydrogenation may be used in sensing hydrogen.
3. The reverse saturation current approaches to the theoretical predication of *I–V* characteristics in Schottky diodes.
4. Raman spectroscopy confirms the presence of hydrogen at the interface of Si/Mn and Si/Co.

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