Hydrogen in semiconductors

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Abstract. Hydrogen in crystalline semiconductors has become a recent curiosity because of its high diffusivity and strong chemical activity in such materials. In contrast to the proton motion in ionic materials which gives rise to an enhanced conductivity, hydrogen in electronic materials interact with structural disorders and chemical impurities to control the electronic flow. Deep gap states in crystalline semiconductors due to various disorders such as surface/interface, grain boundaries, dislocations, irradiation and implantation damage etc. have been removed due to hydrogen bondings.

Hydrogen incorporation is done by plasma and direct ion beam hydrogenation methods, implantation technique and by a novel technique of damage free introduction. The most studied materials are silicon and gallium arsenide. $I - V$, $C - V$, DLTS and IR studies have been carried out on hydrogenated semiconductors to characterize the electronic flow, gap states and the nature of chemical bonds. Improvement in ideality factors of diodes, reduction in free carrier concentration, removal or reduction of deep states and appearance of new bondings such as Si-H, P-H, B-H etc. have been observed from various techniques.

The present paper reviews the various features of hydrogenation studies in crystalline silicon and gallium arsenide and highlights our results of hydrogenation studies on Pd/semiconductor devices.

Keywords. Semiconductor; hydrogen; interface states; passivation.

1. Introduction

Hydrogen in crystalline semiconductor has become a recent curiosity (Pankove and Johnson 1990; Stutzmann and Chevallier 1991; Pearton *et al* 1992). Hydrogen in amorphous semiconductors has already gained significance due to its role in tailoring the materials for any device application. The amorphous semiconductors could not have become technologically viable without hydrogen incorporation which reduces the defective bond density and allows doping in such materials. In polycrystalline semiconductors, hydrogen plays a vital role in passivating grain boundaries which were otherwise sinks for the dopants and killer centres for the photogenerated carriers. The incorporation of hydrogen in crystalline semiconductors has become a subject of intense investigation because of its ability to interact with defects and dopants. It has been found that atomic hydrogen can make bonds at the defective sites to remove the gap states which improves the device performance of such materials. This gave a boost to the research activity in the area of hydrogen in crystalline semiconductors and hence various studies to investigate the different aspects have been carried out. The most widely studied materials are Si and GaAs which are technologically significant. In these materials both donors and acceptors and a wide variety of impurities and defects are deactivated on hydrogenation.

In this paper we review the present status of hydrogenation in Si and GaAs and highlight our novel technique (Srivastava *et al* 1988; Tripathi *et al* 1989) of hydrogenation. Our technique (figure 1) of hydrogenating the semiconductor materials (Si and GaAs) is by making Pd/semiconductor contacts which are kept in an atmosphere of molecular hydrogen. Our technique differs from the usual technique of hydrogenation,

Figure 1. A schematic set up for hydrogenation of Pd/semiconductor by molecular hydrogen.

such as hydrogen plasma exposure and ion-implantation. These techniques of hydrogenation cause damage to the semiconductor substrate due to the high energy whereas our technique is based on the hydrogen diffusion at room temperature.

2. Techniques for atomic hydrogen incorporation

2.1 Hydrogen plasma

The most common method of generating a stream of atomic hydrogen is through the hydrogen plasma. Usually, molecular hydrogen is pumped at a reduced pressure (~ 0.1 Torr) into a quartz tube. The plasma is excited by capacitive or inductive coupling low frequency (~ 30 KHz) or radio frequency (~ 14 MHz) power. Samples are typically heated to 100 to 400 °C for a period of 0.5 to 2 h either downstream or directly immersed in the plasma. This process of hydrogenation results in the hydrogen incorporation to a depth of ~ 50 μm . The plasma exposure technique has the disadvantage that it creates near surface damages due to the presence of energetic ions (~ 100 to 1000 eV) with a flux of $\sim 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ at the plasma edge.

2.2 Hydrogen ion implantation

Hydrogen ion implantation is another technique for incorporating hydrogen in materials. Ion implantation is employed at a energy of 20 to 400 keV. The range of H^+ is ~ 1 μm for 100 keV in GaAs and little more in Si. There is a disadvantage that the implantation energy creates lattice-displacement damages.

Another method of implantation employs a low ion energy (100 to 1000 eV) but a high beam current (1.0 to 6.0 mA/cm^2) for a sufficiently long time to achieve a total dose of $\sim 10^{17} \text{ H}^+$ ions/ cm^2 . The ion source for the purpose is commonly known as Kaufman ion source which is a multiaperture ion source.

2.3 Hydrogenation through Pd/semiconductor devices

A new approach of hydrogenating semiconductor (Si and GaAs) has been adopted (figure 1) in our laboratory. The hydrogenation process is through molecular hydrogen. The decomposition of the H molecules at the surface is difficult and generally limits its introduction into the lattice. This limiting process has been overcome by making Pd/semiconductor devices and putting the devices in the atmosphere of molecular hydrogen. Palladium adsorbs the molecular hydrogen and stores it as atomic hydrogen. This, in turn, diffuses from the palladium film to the Pd/semiconductor interface and towards the bulk semiconductor. This process of hydrogenation does not cause any surface damage or displacement damages because it depends on the diffusion of atomic hydrogen at room temperature. Hydrogenation can also be performed at a little higher temperature of $\sim 60\text{--}70^\circ\text{C}$.

3. Shallow dopants deactivation on hydrogenation

Both shallow donors and acceptors have been found to be deactivated on hydrogenation in Si and GaAs. It has been generally found that on hydrogenation, acceptors are more susceptible to deactivation than donors. The removal of carriers is not due to compensation by the introduction of donors/acceptors but it is deactivated by association of hydrogen with acceptors/donors.

Shallow acceptors like B, Al, Ga, In and Tl in Si have been found to be passivated by association with atomic hydrogen plasma. Shallow donors P, As and Sb have shown a relatively weak deactivation after exposure to atomic hydrogen plasma. The amount of deactivation also depends on the doping levels.

In Pd/Si hydrogenation studies (Srivastava *et al* 1988; Tripathi *et al* 1989, 1992) it has also been found that both acceptor and donor density is reduced on hydrogenation. The donor/acceptor densities has been estimated from $C - V$ studies which is given in table 1. It has been found that in this hydrogenation process too, the acceptors are deactivated to a larger extent than the donors, on hydrogenation.

Shallow acceptor impurities (Be, Mg, Cd, Zn and C) and shallow donor impurities (Si, Ge, Sn, Se and Te) in GaAs have been found to be passivated on association with atomic hydrogen (Johnson *et al* 1986a, b; Chevallier *et al* 1988; Pearton *et al* 1992). It has been observed that the plasma hydrogenation causes a strong reduction in shallow carrier density in the near surface region. The depth of such surface modifications has

Table 1. Carrier concentration ($\times 10^{16}\text{ cm}^{-3}$) for *n* and *p* silicon substrates, before and after the hydrogenation of Pd/Si.

Frequency	Unhydrogenated		Hydrogenated	
	<i>n</i> -type	<i>p</i> -type	<i>n</i> -type	<i>p</i> -type
1 MHz	3.6	—	2.0	—
100 KHz	3.6	6.8	2.3	2.6
40 KHz	—	6.9	—	2.7
10 KHz	5.2	7.7	3.6	2.9
1 KHz	6.5	—	4.0	—

Table 2. Carrier concentration ($\times 10^{16} \text{ cm}^{-3}$) for *n* and *p* GaAs substrates, before and after the hydrogenation of Pd/GaAs.

Frequency	Unhydrogenated		Hydrogenated	
	<i>n</i> -type	<i>p</i> -type	<i>n</i> -type	<i>p</i> -type
10 KHz	3.18	75.0	1.16	6.40
100 KHz	1.18	10.0	0.92	3.10
1 MHz	0.90	—	0.62	—

Figure 2. The carrier profile of *n*-GaAs from *C-V* studies of Pd/*n*-GaAs, before and after the hydrogenation.

been found to be inversely proportional to the initial doping levels. The passivation depth has also been found to vary as square root of the plasma-exposure time, which shows an indiffusion process.

In the hydrogenation studies of Pd/GaAs, both donor and acceptor density has been found to be reduced (table 2) on hydrogenation. The reduction of donor density is by 30% whereas of acceptor is by 70%. The depth profile (figure 2), obtained from the *C-V* studies of Pd/*n*-GaAs Srivastava *et al* (1991), shows that the donors (Si) are reduced up to a depth of $\sim 0.5 \mu\text{m}$ on hydrogenation.

4. Effect of hydrogen on deep levels

Deep levels related to various chemical impurities and structural disorders have been found to be influenced both in the near surface/interfacial and bulk regions on hydrogenation. The deep levels usually reduce the minority carrier lifetime in the semiconductor material. Moreover, the breakdown voltage of Schottky diode or *p-n* junction reduces and the reverse leakage current increases due to the presence of deep levels. The passivation of deep levels on hydrogenation in crystalline semiconductors gave a hope that the deleterious features in the devices could be tackled. Improved opto-electronic efficiency and reliability in the devices has been achieved due to

Table 3. Deep levels passivated by hydrogen in different materials of GaAs.

GaAs	Energy (eV) from CB edge
LEC	0.16, 0.24, 0.36, 0.82 (EL2)
LPE	0.13, 0.38, 0.54, 0.73
MBE	0.17, 0.28, 0.45
Polycrystalline	0.36

hydrogenation. However, the thermal stability of the hydrogen related complexes is not sufficient enough to make hydrogenation useful in all applications. For example, the well known gold acceptor ($E_c - 0.54$ eV) (Pearton and Tavandale 1982) was passivated to a depth $> 10 \mu\text{m}$ and was partially regenerated on a subsequent vacuum anneal at 400°C .

Deep levels due to metallic impurities (Au, Fe, Ni, Cu, Pd, Mo) which are typically introduced into Si wafers during high temperature processing steps could be passivated on hydrogenation. The effect of hydrogenation on deep levels have been typically studied by DLTS (deep level transient spectroscopy) (Lang 1974) technique. The technique gives the signature of deep levels of the crystalline materials with a sensitivity, to measure the deep level concentration, of one part per million of shallow dopants. The technique can distinguish the electron and hole traps and so is successfully employed for acceptors and donors in *p*-type and *n*-type materials. There is enormous data on the hydrogen passivation of various contaminants and induced impurities which show the role played by hydrogen in electronic materials (Pearton *et al* 1992).

Another type of defect, giving rise to gap states, is related to the processes induced in the materials. For example, the processes in which the electrically active defects (deep levels) are introduced are etching (chemical, reactive ion and sputter), annealing (laser and thermal), quenching, ion-implantation and irradiation with photons or particles with energies sufficient enough to cause atomic displacements. All such deep levels have been influenced on hydrogenation to show a hydrogen passivating effect (Pearton 1982; Singh *et al* 1984; Mu *et al* 1986a, b; Pearton *et al* 1992).

The main defect in liquid encapsulated Czochralski (LEC) GaAs which is particularly known as EL2 centre (an As antisite defect, As_{Ga}) and which causes a compensation of acceptors has been shown to be passivated by atomic hydrogen (Lagowaski *et al* 1982). Table 3 shows the various deep levels passivated by hydrogen in different materials of GaAs.

Deep levels in GaAs substrates have also been found to be influenced on hydrogenation of Pd/GaAs devices. From $C - V$ and TSCAP (thermally stimulated capacitance) studies it has been found that the density of donor states at 0.48 and 0.75 eV and density of 0.69 eV acceptors are reduced on hydrogenation (Singh 1993).

5. Mechanism of hydrogen interactions with donors/acceptors

Atomic hydrogen typically goes into the interstitials of the silicon lattice and diffuses fast until it is trapped at a defect or impurity site or paired to form a molecule ($\text{H}^0 + \text{H}^0 = \text{H}_2$). However, ion channeling experiments (Wieringen and Warmoltz

Figure 3. The various sites for hydrogen in silicon lattice. BC (bond centred), AB (anti-bonding) and T_d (tetrahedral interstitial) (Deak *et al* 1988).

1956) on deuterium-implanted Si showed that most of the deuterium was located at a unique site which is displaced by $\sim 1.6 \text{ \AA}$ from a Si atom along (111) direction away from the neighbouring atom, known as the antibonding site (AB). Singh *et al* (1977) showed from their theoretical calculations that the equilibrium position for atomic hydrogen in a perfect lattice was the tetrahedral interstitial site (T_d).

There are several possible sites for the atomic hydrogen in a semiconductor material which depends on the conductivity type of the material. For example, typically atomic hydrogen occupies the bond centre (BC) site in *p*-Si and AB site in *n*-Si (figure 3). In *p*-type Si the atomic hydrogen was found to be in H^+ form, exhibiting a donor-like behaviour. The H^+ is not a bare proton but somewhat delocalized due to the charge exchange with the Si lattice. In *n*-type Si, either H^0 or H^- are the most stable form which cause passivation effects (Srivastava *et al* 1992). Van de Walle *et al* (1989) from their theoretical calculations found that the BC site is the global minimum for the neutral and positive charge states of hydrogen in Si whereas the near- T_d site is favoured for the negative charge (H^-).

Acceptor passivation occurs (Pantelides 1987) first by compensation in which the electrons from the neutral hydrogen atoms recombine with free holes, as shown below

The reaction for donor passivation when phosphorous is the donor is shown as below (Chang and Chadi 1989)

Formation of neutral complexes $(BH)^0$ and $(HP)^0$ on hydrogenation result in dopant deactivation.

The passivation by atomic hydrogen of both shallow acceptors and donors in GaAs and its diffusion characteristics indicate that the H^+ are the likely species in *p*-GaAs, and H^0 or H^- are in *n*-type GaAs. The possible mechanism for the impurity passivation in *n*-type GaAs is the bonding of hydrogen with the donor (figure 4) and in *p*-type it is

Figure 4. (a) The hydrogen complexation in *p*-GaAs and (b) the hydrogen complexation in *n*-GaAs, as referred in text.

the formation of As–H bond adjacent to the Ga-site acceptor (figure 4) (Nandhra *et al* 1988; Chang 1991).

6. IR spectroscopy of hydrogenated materials

IR spectroscopic studies were carried out to identify the complexes formed on hydrogenation and also to reveal the mechanism of hydrogen induced deactivation of donors/acceptors.

Room temperature IR spectroscopy of hydrogen plasma passivated B-doped silicon showed the vibrational band at 1875 cm^{-1} (Johnson 1985; Pankove *et al* 1985). In

Pd/*p*-Si hydrogenated devices, we observed a vibrational band around 1870 cm^{-1} (Tripathi *et al* 1992). The vibrational frequency has been related to the bond centred (BC) hydrogen in Si–H–B configuration. There have been several theoretical studies to confirm such bonding configuration for an equilibrium situation (Pearton *et al* 1992).

For *n*-silicon there has been a IR study for hydrogen plasma treated, As, P and Sb doped silicon (Bergman *et al* 1988). They observed a sharp absorption line near 1560 cm^{-1} which shifted to 809 cm^{-1} on the exposure to deuterium plasma. The shift with deuterium confirmed that the particular peak is related to the hydrogen donor complex.

In our IR study (figure 5) of the hydrogenated Pd/*n*-Si (Tripathi *et al* 1989), we found that there are vibrational bonds near 2340 cm^{-1} , 2100 cm^{-1} and also a band near 1570 cm^{-1} . We related the 2340 cm^{-1} to P–H complex and 2100 cm^{-1} to Si–H complex. The 1570 cm^{-1} vibrations are related to the Si–H complexes as observed by Bergmann *et al* (1988). We recorded the IR spectra of Pd/*n*-Si for nearly a month after the hydrogenation to monitor the growth of absorption peaks. Figure 6 shows that the absorption peaks grow linearly with time which indicates the indiffusion of hydrogen. Theoretical models were given (Johnson *et al* 1986; Bonapasta *et al* 1989) which showed the 2100 cm^{-1} frequency for the hydrogen bounded at an anti-bonding site. Later it has been shown that for Si–H bond length of $1.41\text{ \AA}$ the vibrational frequency is 2149 cm^{-1} whereas the Si–H bond length of $1.66\text{ \AA}$ results in vibrational mode of 1460 cm^{-1} . It seems that both the configurations are possible for donor–H complexes which results in donor deactivation (Denteneer *et al* 1990; Zhang and Chadi 1990).

The hydrogen interaction in GaAs lattice is more complicated as compared to Si because of the two sublattices. Moreover, the acceptors/donors can be at Ga site or As site and so several hydrogen induced complexation are observed. For *n*-GaAs with silicon donors at gallium sites, i.e. GaAs:Si_{Ga}, IR spectroscopy (Pajot *et al* 1988) reveals the stretch frequency of 1717.3 cm^{-1} which has been configured as H attached directly to Si_{Ga} atom in an antibonding direction. There have been numerous studies of IR on *p*-GaAs with acceptor at gallium site and at arsenic sites (Pearton *et al* 1992). It was proposed that the H is at the BC site between the acceptor (e.g. Zn) and one of its As neighbours. The frequency of the H-stretching bond (2116 cm^{-1}) is close to that of

Figure 5. IR spectra recorded at room temperature of hydrogenated Pd/*n*-Si structure. The arrow marks show the vibrational frequencies at 2340 , 2100 and 1570 cm^{-1} .

Figure 6. The growth of absorbance for 2340, 1570 and 2100 cm^{-1} vibrations with the days elapsed after the hydrogenation of Pd/n-Si structures.

As- H. However, for acceptors at the arsenic sites (such as C, Si and Ge), the IR studies suggested a different configuration for hydrogen induced complexes. In this case, H occupies the BC site but it is attached primarily to the acceptor. The trend in the vibrational frequency for the different As-site acceptors in the complexes supports the fact that the H is bonded more strongly to the acceptor than for H complexed with the Ga-site acceptors.

7. Device applications

Hydrogenation of crystalline semiconductors has been found useful in device processing, such as annealing in hydrogen ambient at high temperatures ($\sim 800^\circ\text{C}$) which outdiffuses the native defects from the GaAs.

The hydrogen ion-implantation through the metal over layers (Yaspir *et al* 1988) into the metal/semiconductor interfacial region of the device, has been found useful to control the electronic flow in such devices. It has been found that the implanted hydrogen interacts with the interfacial defects to passivate them and improve the device performance.

In a study of low energy ion implantation (Srivastava *et al* 1994), hydrogen ions ($\sim 100\text{ eV}$) were implanted on the semiconductor surface (prior to the metallization in the metal/semiconductor device) by using a Kaufman ion source. It has been found that the devices realised to such implanted substrates show better and stable characteristics.

Hydrogenation has also been used to realise a new class of field effect transistors, known as HFET (hydrogenated field effect transistors), with a graded dopant profile which was achieved by exposing an n^+ GaAs epitaxial layer to a hydrogen plasma. The graded doping profile results in a higher breakdown voltage as compared to normal FET structures. A bandwidth of 15 GHz was achieved at source drain voltage of 2 V with a g_m of 330 ms/mm (Constant *et al* 1987).

Pd based M/S and MOS structures are being used as hydrogen sensing devices since the electronic property of the devices changes significantly on hydrogenation (Lundstrom 1981; Kermati and Zemel 1982; Singh *et al* 1994).

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