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Recombination via transition metals in solar silicon: The significance of hydrogen–metal reactions and lattice sites of metal atoms

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The move toward lower cost sources of solar silicon has intensified the efforts to investigate the possibilities of passivating or reducing the recombination activity caused by deep states associated with transition metals. This is particularly important for the case of the slow diffusing metals early in the periodic sequence which are not removed by conventional gettering. In this paper, we examine reactions between hydrogen and transition metals and discuss the possibility of such reactions during cell processing. We analyse the case of hydrogenation of iron in p-type Si and show that FeH can form under non-equilibrium conditions. We consider the electrical activity of the slow diffusing metals Ti, V, and Mo, how this is affected in the presence of hydrogen, and the stability of TM-H complexes formed. Finally, we discuss recent experiments which indicate that re-siting of some transition metals from the interstitial to substitutional site is

possible in the presence of excess vacancies, leading to a reduction in recombination activity.

12											13
Mg											Al
20	21	22	23	24	25	26	27	28	29	30	31
Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
38	39	40	41	42	43	44	45	46	47	48	49
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
56	57	72	73	74	75	76	77	78	79	80	81
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl

Periodic ordering of the 3d, 4d, and 5d transition metals with adjacent columns of the periodic table. The metals with hydrogen complexes which have had their electronic properties reported in the literature or in this paper are highlighted in green.

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1 Introduction In silicon technologies much attention has been devoted to contamination by transition metals (TM), particularly those in the 3d series. These metals are responsible for yield reducing problems associated with, for example, generation currents in MOS devices and dielectric breakdown [1]. In the case of device fabrication using electronic grade silicon, the concern is largely associated with metals introduced during device processing, electronic

grade silicon in its as-grown state contains negligible concentrations of transition metals. This is because it derives from polycrystalline feedstock which has been chemically purified very effectively, for example by the Siemens process, and then is converted to single crystal from the melt usually by the Czochralski (Cz) method. The effective segregation coefficient of transition metals between the solid and the liquid phase of the silicon during

Cz growth is typically $<10^{-5}$ resulting in most of the TMs remaining in the melt rather than being transferred to the grown crystal. The combination of the Siemens process and Cz growth usually results in extremely low and technologically unimportant concentrations of TMs, typically these are $\leq 10^{10} \text{ cm}^{-3}$.

In the case of Solar Silicon, the cost of the silicon is much more important than in the case of electronic grade material applications in microelectronics and so cheaper methods of ingot growth are often used. Many variants on the theme are in production or in development but the end result is that the chemical purification of the feedstock is simplified, for example upgraded metallurgical silicon (UMG) is used, or the inherent purification of the Czochralski method is eliminated using casting. This results in a higher concentration of transition metals in the slices used for solar cell fabrication than in electronic grade Si.

The significance of specific TMs in solar cells was studied in the 1970's in what is now known as "The Westinghouse Experiment." In this work, various concentrations of TMs were added to the melt in a conventional Cz growth procedure and the effect on the solar cell efficiency was measured. The study was an extremely comprehensive one, involving the growth of over 200 TM doped Cz ingots in which the chemical concentrations were measured using neutron activation analysis (NAA), the electrical activity using deep level transient spectroscopy (DLTS), and the detailed effect on the solar cell performance monitored [2].

Families of graphs were published showing the degradation of efficiency as a function of the TM concentration in the p and n-type Si slices used to fabricate the cells, and this was widely referenced showing that certain metals were the most "dangerous." When the results are analysed, it becomes apparent that the order of significance is, in general, the order of the TMs diffusivities (fast diffusers are the least significant in degrading the cell efficiency) and is not solely related to the recombination activity of specific transition metals as was originally proposed [3]. The cell fabrication process used in the Westinghouse experiment used single crystal material and included a very effective implementation of gettering. A similar sequence of experiments on multi-crystalline silicon was undertaken more recently and again, slow diffusers were found to be the most pernicious [4, 5]. The essential conclusion is that contamination with the slow diffusing TMs is particularly detrimental. These correspond to the lower atomic number elements in the 3d and 4d series sometimes referred to as the early 3d and 4d elements. If high efficiencies are to be obtained with less pure silicon which contains these slow diffusing TMs it is important to find ways in which their recombination activity is reduced or eliminated in both single crystal and multi-crystalline materials.

It is well known that reactions between hydrogen and some TMs in silicon can result in passivation or reduced recombination activity. In general, the bonding between hydrogen and the TM is weak ($\sim 2 \text{ eV}$) and so the hydrogen is dissociated at temperatures well below those experienced in solar cell processing. In addition, in p-type

material hydrogen-TM reactions are usually inhibited by Coulombic repulsion. Despite this, recent work has indicated that substantial improvements in lifetime of both Cz and cast UMG p-type solar silicon can be achieved through hydrogen treatments in which light is used. This is interpreted as being due to a change in the charge state of the hydrogen [6]. In this paper, we consider these issues and present some of our recent work on the hydrogenation of TMs and also, evidence for displacement of some TMs from the interstitial to substitutional site. In conjunction with earlier work on hydrogenation we try to draw generalisations in relation to the mechanism of hydrogen passivation and its stability. Our principal tools in these studies have been DLTS and related analytical techniques which we describe elsewhere [7].

2 Formation and thermal stability of hydrogen-TM complexes in silicon

2.1 TM-H reactions in p-type Si

Hydrogen atoms are very mobile in silicon at room temperature and atomic hydrogen is likely to combine with impurities and intrinsic defects [8]. The initial hydrogen reaction is highly dependent on the charge state relative to the defect or impurity. Predominantly, the reaction is driven by long range Coulombic interactions. Atomic hydrogen is an amphoteric impurity with negative-U ordered donor and acceptor levels at $E_c - 0.18 \text{ eV}$ and $\sim E_c - 0.65 \text{ eV}$. The neutral state is metastable. Isolated hydrogen occurs in the positive charge state in p-type Si, while it is negatively charged in n-type. As the $\text{H}^{(+/-)}$ occupancy level lies in the upper half of the band gap it would be expected that in intrinsic Si (mid-gap Fermi level) the H^+ charge state will dominate. Experimentally, there is evidence that H^- is the stable form when the Fermi level is $>0.3 \text{ eV}$ above the mid gap energy [9].

The fact that hydrogen is positively charged in p-type Si explains why there are many reports of TM-H complexes in n-type Si, whereas there are none in equilibrium in p-type Si. The interstitial TMs tend to be positively charged in p-type and hence there will be Coulombic repulsion between the metal and the hydrogen. Under these conditions the metal-hydrogen complex will not form. However, if the Fermi level can be manipulated or an adequate flux of minority carriers generated, non-equilibrium charge states can be attained and some reactions with H may now become possible.

We have explored this concept by forcing a hydrogen reaction with iron in p-type Si. Previously a Fe_2H complex has been characterised in n-type Si as a hole trap with an energy level at 0.31 eV above the valence band [10]. *Ab initio* calculations have predicted that the Fe_2H complex should be stable at room temperature and have a deep donor level at about $E^v + 0.40 \text{ eV}$ and a deep acceptor level at about $E_c - 0.3 \text{ eV}$ [11].

We took Fe contaminated $12 \Omega \cdot \text{cm}$ p-type Cz-Si samples and introduced hydrogen either from a hydrogen-rich silicon nitride layer or by wet etching [12]. The DLTS spectrum for a Fe contaminated and hydrogenated sample is shown in Fig. 1 as line 1, as measured on a Schottky diode evaporated onto an unheated sample. A peak

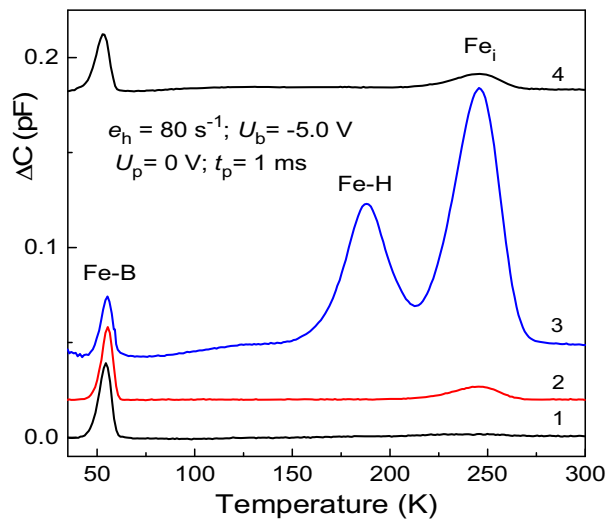


Figure 1 DLTS spectra of Fe contaminated p-type Cz-Si samples with Fe_i concentration $1.3 \times 10^{13} \text{ cm}^{-3}$ 1) before annealing, 2) after annealing at 110°C without bias, 3) after annealing at 110°C with 5 V reverse bias, and 4) followed by annealing at 175°C for 30 min without bias.

with its maximum at about 55 K, clearly identifiable as related to the Fe-B pair, is evident. If the sample is annealed at 110°C with zero bias a small peak with its maximum at about 245 K due to Fe_i appears (line 2). If, however, the same anneal is undertaken with the Schottky diode under 5 V reverse bias in the DLTS spectrum (line 3) the Fe_i related signal becomes much more prominent and a trap with characteristics identical to that ascribed to Fe_iH in n-type Si is seen.

This is because the 5 V reverse bias establishes a near intrinsic depletion region in which the defect reactions occur. This region is probed in subsequent DLTS scans. Many things are happening during this anneal including the drift of the hydrogen in the electric field toward the bulk of the semiconductor. This can be measured by observing the passivation of the boron acceptors deeper in the bulk using traditional CV measurements. This would indicate that the hydrogen remains positively charged in the depletion region as expected from the fact that the hydrogen converts to H^- only when the Fermi level rises to 0.3 eV above the mid gap energy [9]. Fe_i with its donor level at about 0.4 eV above the valence band becomes neutral in the depletion region and so, that switches off the attractive Coulomb field of B^- for Fe_i^+ occurring in the bulk. Now, the neutral Fe atoms escaping from the boron at 110°C are not recaptured by boron (this explains the large increase in the Fe_i related DLTS signal in the spectrum 3 in Fig. 1) and are free to interact with H^+ .

If this interpretation is correct, then it is evident that whether or not the pairing reaction occurs depends on the charge state of the TM in the depletion region in p-type Si which depends on its 0/+ energy level position and so is species specific.

Titanium and vanadium interstitial atoms have their first donor levels in the upper half of the Si gap at about $E_c-0.27 \text{ eV}$ and $E_c-0.45 \text{ eV}$, respectively [3]. As the Ti_i and V_i atoms are always positively charged in p-type Si, the interactions of these atoms with positively charged H atoms are very unlikely in p-type material. Indeed, we have not observed any changes in the DLTS spectra of p-Si crystals, which were contaminated with Ti and V impurities, after hydrogenation [13, 14].

The case of Mo contaminated p-type Si crystals is more complicated. Molybdenum is arguably the most potentially harmful metallic impurity considered in this work, seen to significantly reduce carrier lifetime and correspondingly cell efficiency at lower concentrations than Ti and V [2]. It is also practically impossible to getter [15] and has not been observed to form large precipitates, although recent work [16] has shown nanoscale precipitates of Mo can form and act as very efficient recombination centers.

The majority of electrically active Mo in silicon is found at an interstitial site and is known to introduce one deep donor level in the silicon band gap close to $E_v + 0.30 \text{ eV}$ [2, 3]. Some evidence has been presented of Mo-related levels in the upper half of the gap [17, 18]. However, the most recent study of these levels [18] suggests that these are not likely to be due to the Mo interstitial. In previous DLTS studies of Mo in p-type material, as well as in our work to date, no evidence of Mo-H complexes has been observed. However, the unidentified DLTS signals related to Mo in the upper half of the gap, which were observed in Refs. [17, 18], could be related to Mo-H complexes.

It is to be expected that a shift in Fermi level and hence modification of the charge state could be achieved through illumination with above band gap light so generating minority carriers as implemented in Ref. [6]. However, the situation is much more complex than the Fermi level shift due to changes in bias in our experiments above. This is primarily due to the presence of both minority and majority carriers and their direct reactions with the defects to produce non-equilibrium charge states.

2.2 TM-H reactions in n-type Si In n-type material hydrogen atoms are negatively charged and can travel along the lattice through sites with low electron density (tetrahedral and hexagonal sites). In this situation, TM interstitials are likely to be either neutral or positively charged, increasing the probability of TM-H reactions. A few examples of such interactions are presented below.

2.2.1 Titanium Interstitial titanium in silicon, located at the tetrahedral interstitial lattice site, presents three levels in the silicon band gap at $E_c-0.08 \text{ eV}$, $E_c-0.27 \text{ eV}$, and $E_v + 0.26 \text{ eV}$ [3]. Despite early results suggesting that hydrogen passivation would only be effective for fast diffusing transition metals, recent studies have shown the formation of $Ti-H_n$ complexes in n-type Si [13, 19, 20].

In our recent work [13], samples of n-type Si implanted with Ti and annealed were treated with a remote hydrogen

plasma at room temperature. In these conditions, titanium was shown to form at least three Ti-H_n complexes with electrically active levels in the silicon band gap, with some formation of electrically inactive complexes. When annealed at relatively low temperatures (100–150 °C), the concentration of these electrically active Ti and Ti-H_n complexes was reduced until almost complete passivation of Ti was observed. DLTS spectra of Ti implanted n-type Cz Si are shown in Fig 2 before and after hydrogenation and subsequent annealing. In the DLTS spectrum of as-implanted samples (spectrum 1 in Fig. 2), two strong peaks with their maxima at about 40 and 150 K corresponding to interstitial Ti are seen. After a treatment with a hydrogen plasma (spectrum 2), new signals corresponding to various Ti-H_n complexes are observed modifying the shape of the 150 K peak and are components of the peak at ~270 K. Crucially, after annealing the hydrogenated samples at 100–150 °C (spectra 3 and 4) all of the Ti and Ti-H_n related signals in DLTS are significantly reduced, indicating the formation of an electrically inactive Ti-H complex with no levels in the Si band gap. These complexes are unstable at higher temperatures and nearly a complete recovery of all electrically active Ti was seen after annealing at 250 °C.

2.2.2 Vanadium Interstitial vanadium, like titanium, is situated at the tetrahedral interstitial lattice site and can cause severe reductions in cell efficiencies at concentrations as low as 10¹² cm⁻³. It presents three deep level states in the silicon band gap at $E_c - 0.20$ eV, $E_c - 0.45$ eV, and $E_v + 0.34$ eV [3]. In n-type silicon, interstitial vanadium has been shown experimentally to interact with hydrogen and

form at least one well documented electrically active vanadium hydrogen complex at about 0.51 eV from the conduction band [14, 21].

The behaviour of this V-H complex following various thermal treatments is documented in Ref. [14]. The concentration of V-H complexes was shown to be increased upon annealing at temperatures between 75 and 150 °C, with a complete recovery of the interstitial vanadium concentration at temperatures above 175 °C. The behaviour of V-H complexes is illustrated in Fig. 3, which shows the concentration of V and V-H traps after various processing conditions, as well as their DLTS spectra. The depth profiles were obtained from an analysis of the Laplace DLTS spectra recorded with variable reverse bias and filling pulse voltages. The effect of the Debye tail was taken into account. As can be seen in Fig. 3, in the presence of hydrogen the total concentration of electrically active vanadium related complexes is reduced, indicating the formation of electrically inactive complexes involving vanadium and hydrogen.

2.3 Structures of TM-H complexes Depth profile studies of TM-H-related DLTS signals [13, 14, 20] along with *ab initio* calculations [22] strongly indicate the formation of electrically active TM-H_n complexes that result from the capture of $n \geq 1$ hydrogen atoms. Ti is a prominent example, it seems to be able to bind with up to four H atoms and become electrically inert.

Concerning the defect structure, for $n = 1$, titanium- and vanadium- and molybdenum-hydrogen complexes form trigonal structures like the one depicted in Fig. 4, with the

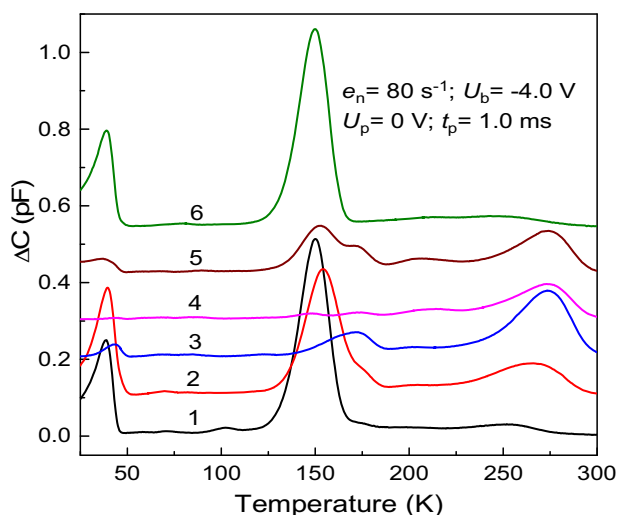


Figure 2 DLTS spectra for a Ti implanted n-type Cz-Si sample taken after (1) 30 min annealing at 650 °C in N₂ gas ambient, (2) subsequent hydrogen plasma treatment at room temperature, and (3)–(6) 30 min isochronal annealing in the temperature range 100–250 °C with 50 °C increments. Measurement settings are shown on the graph.

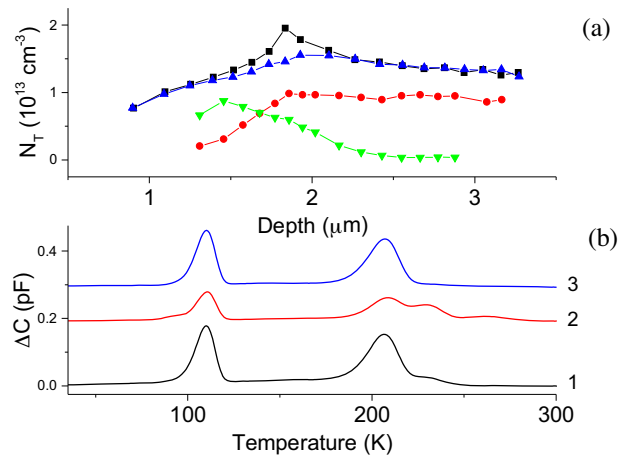


Figure 3 (a) Concentration-depth plots of interstitial vanadium in V implanted n-type Si after implantation and 800 °C annealing (black), after H-plasma treatment (red) and subsequent annealing at 200 °C (blue). The concentration of an observed electrically active V-H complex is shown (green) as present immediately after H-plasma treatment. (b) DLTS spectra for (1) the V-implanted n-type Si sample, which was annealed at 800 °C for 30 min in Ar gas ambient, (2) the similarly treated neighbouring sample, which was subjected to an H-plasma treatment, and (3) subsequently annealed at 200 °C.

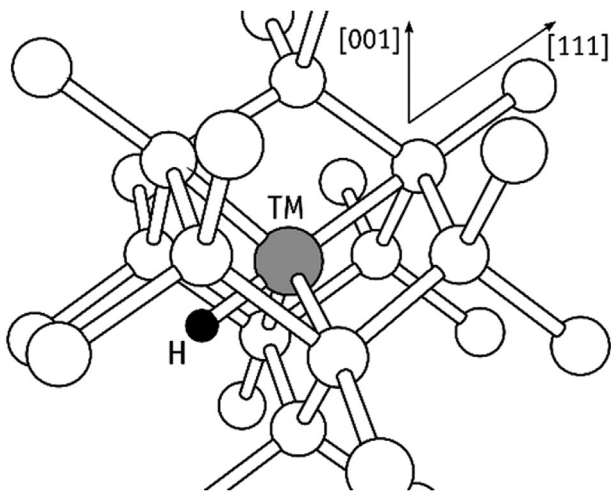


Figure 4 Atomistic model of an interstitial transition metal connected to an H atom. Si, H, and the TM are shown in white, black, and grey, respectively.

metallic ion remaining close to the tetrahedral site and hydrogen located near the hexagonal site along the $\langle 111 \rangle$ axis [22–24]. For the specific case of Ti, further H attachment at equivalent sites is energetically favourable. We found that the number of hydrogen atoms that Ti is able to getter depends on the position of the Fermi-level: while in *p*-type material the formation of Ti-H_n complexes is hindered due to electrostatic repulsion. Once we move into intrinsic and *n*-type Si, the binding of hydrogen to Ti becomes energetically favourable and the maximum number of H atoms that have a positive binding energy increases as the Fermi level rises in the gap. A similar behaviour was also obtained for other early metals such as vanadium or molybdenum (at least up to TM-H_2), which like titanium, possess deep donor levels within the band gap [25]. The increase in the number of hydrogen atoms connected to the TM ion leads to a shift or a gradual removal of the electronic states. For the Ti interstitial, a single donor is left for $n = 3$, while full passivation is obtained for $n = 4$.

2.4 Thermal Stability of TM-H complexes and hydrogen charge state manipulations In both *p*-type and *n*-type Si the binding of hydrogen to the metal, in the cases we have examined, is rather weak, typically $< 2 \text{ eV}$. This implies that the hydrogenated fraction of the TMs resulting from their reactions with hydrogen is diminishingly small in Si above 200°C . Although high temperatures are necessary to establish an adequate concentration of hydrogen throughout a silicon slice, our expectation is that the published process of carrier lifetime improvement by illumination is only significant during the cooling cycle and is in competition with other hydrogen reactions and the formation of molecular hydrogen in the silicon.

3 Lattice site changes as a route for reduced recombination While formation of complexes of

transition metals and hydrogen has been shown to be effective for reducing the electrical activity of transition metals in silicon, it is also possible to render slow diffusing impurities inactive by displacing them to the substitutional site.

To date, we have shown this effect to occur for two of the three transition metals discussed so far in this paper, titanium and vanadium, when excess vacancies are introduced by implantation [26, 27]. For both of these metals, displacement to the substitutional site has been observed in float zone silicon implanted with metal ions after annealing at high temperature. When comparing SIMS measurements of the total metallurgical concentration of the TM atoms to the concentration of interstitial TM's measured electrically with DLTS, a significant difference is observed between float zone grown and Czochralski grown silicon crystals after annealing.

In float zone silicon, after annealing, the electrically active fraction was seen to be smaller than the total metallurgical concentration, suggesting that the majority of the impurity atoms are not located at the interstitial site. In Cz-Si the ratio of metallurgical concentration to interstitial concentration was much closer. As well as this, redistribution of impurity atoms away from the implant site was shown to occur much more readily in Cz-Si than FZ-Si, suggesting greater diffusivity of metal atoms in this material. As no evidence of precipitation was observed in either the Cz or float zone Si samples, it was concluded that a significant fraction of TM atoms had been moved to the substitutional site in float zone silicon. At this site, these atoms have a significantly lower diffusivity, accounting for the discrepancy in redistribution between the two materials. It was also concluded that as no further evidence of electrical activity was observed either in capacitance-voltage measurements or in DLTS that the TM atoms are electrically inactive at this site [26, 27].

The difference between the two materials is assumed to be primarily due to the different concentrations of available implantation induced vacancies in Cz and FZ Si. In Cz Si, vacancies are known to interact with oxygen, which is typically present at concentrations as high as 10^{18} cm^{-3} , forming vacancy oxygen complexes, which are stable up to temperatures as high as 700°C [28]. As the concentration of oxygen is so much higher than that of the metallic impurities, it is unlikely that interstitial impurity atoms will interact with vacancies during annealing. In contrast, in float zone silicon the concentration of oxygen is much lower, and so displacement of metal atoms to the substitutional site can occur, accounting for the differences observed in our measurements.

5 Conclusions We have examined reactions between hydrogen and TMs in silicon. In *p*-type material we identify the lack of observations of TM-H complexes as being due to long range Coulombic repulsion between the positively charged hydrogen and the positively charged TM. However, we have demonstrated that it is possible to form FeH

complexes in p-type material in the depletion region of a Schottky diode. This is attributed to the formation of the neutral charge state of the Fe_i donor in the depletion region reacting with H^+ . We present evidence that in our experiments (without light on the samples) the hydrogen is always in the positive charge state in the depletion region of p-type Si. Further, it is found that not all transition metals react with hydrogen under these conditions and we hypothesise that a reaction will not take place if the $\text{TM}^{0/+}$ energy level is above the Fermi level and hence retains the positive charge state in the depletion region.

We have considered the formation of TM-H complexes with multiple hydrogen atoms and conclude that in intrinsic and n-type Si, the binding of hydrogen to Ti becomes energetically favourable, and the maximum number of H atoms that have a positive binding energy increases as the Fermi level raises in the gap. A similar behaviour is also predicted for other early metals such as vanadium or molybdenum (at least up to TM-H_2), which like Ti, possess deep donor levels within the band gap.

Measurements of the thermal stability in all cases for the TMs show weak binding energy of H atoms of ~ 2 eV which results in their dissociation above $\sim 200^\circ\text{C}$. However if hydrogen is trapped in the silicon the TM-H complexes can reform on cooling.

Finally, we have investigated the behaviour of Ti and V in the presence of excess vacancies and compared the TM behavior in FZ and Cz materials. We see a reduction of electrical activity (partial passivation) and a reduction in diffusivity in FZ material when excess vacancies are present. The effect does not occur in Cz material due to the preferential reaction of the vacancies with the oxygen in Cz Si. We attribute this change of diffusivity and passivation to re-siting of the TM from interstitial to substitutional positions in the lattice.

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