

Evidence for Molybdenum-Hydrogen Bonding in p-Type Silicon upon Annealing under Illumination

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Transition metals (TMs) are common contaminants in solar silicon produced by block casting or using lower grade polysilicon feedstock. Gettering can effectively remove certain metals, but slow diffusing TMs can remain and act as highly efficient recombination centers. One method to reduce their recombination activity is hydrogen passivation, however, this is generally ineffective in p-type silicon, in which hydrogen and TMs are typically both in positive charge states. Recent studies have suggested that under illumination, the charge state of hydrogen in silicon can be altered, and its bonding with certain defects can be enhanced. In this work, deep level transient spectroscopy (DLTS), Laplace DLTS, and capacitance-voltage measurements are used to study TM-H bonding in p-type silicon intentionally contaminated with Mo and hydrogenated via remote H plasma. It is found that heat-treatments at moderate temperatures ($<250^{\circ}\text{C}$) under illumination with an LED at 850 nm result in a reduction in the concentration of electrically active Mo, with no similar reduction seen in samples annealed in the dark. The passivated fraction of Mo can be recovered after dark annealing at temperatures $>200^{\circ}\text{C}$. The results obtained provide evidence that upon heat-treatments with illumination Mo-H bonding in p-type Si occurs. Possible mechanisms of the observed effects are discussed.

1. Introduction

Transition metals are common contaminants of crystalline silicon, and can be introduced by various means during crystal growth and device processing. Transition metals typically introduce deep level states in the silicon band gap, which can be highly recombination efficient, and can have disastrous effects on carrier lifetime, even at extremely low concentrations ($\leq 10^{12}\text{ cm}^{-3}$ for certain metals^[1,2]). Transition metal contamination can be important for applications where the cost of silicon must remain low, such as in the production of silicon solar cells, where material growth methods with poor impurity segregation, or lower quality polysilicon feedstock, are often used. These

growth processes can result in greater concentrations of metallic impurities than those contained in electronic grade single crystal materials. In some solar grade silicon TM concentrations of 10^{12} – 10^{16} cm^{-3} have been found to be present.^[3,4]

Although the concentration of electrically active fractions of certain transition metals such as iron and chromium can be reduced through gettering or the formation of precipitates, slow diffusing metals, such as Ti, V, and Mo, are extremely insensitive to either process,^[5,6] and as a result are found to have the most detrimental effect on carrier lifetime, and hence cell efficiency.^[1,2,5]


As a result, other methods such as chemical passivation are required in order to reduce their deleterious effects. One established method of reducing the recombination activity of defects in silicon is the introduction of atomic hydrogen into the material. Hydrogen atoms can bond to a wide range of recombination active defects and alter their electrical activity. The interactions between electrically active

defects, including transition metals, and hydrogen have been studied in some detail, with electrically active and passive transition metal-hydrogen complexes seen for around a dozen metals (see, e.g., Refs. [7–22]).

In general, however, at room temperature in equilibrium conditions TM-H complexes are only seen to form in n-type Si where hydrogen has been shown to be in the negative charge state,^[23,24] while interstitial transition metal atoms are typically neutral or positively charged. In p-type Si, similarly positively charged hydrogen and transition metal atoms experience Coulombic repulsion, and TM-H complexes are not seen to form. A plot of the known electrically active states of a range of transition metals, as well as hydrogen is shown in Figure 1.

Under non-equilibrium conditions the charge state of defects can be altered, allowing the formation of TM-H complexes in p-type Si. This can be achieved either by shifting the Fermi level, or by generating a significant flux of minority carriers. In practice in Si devices, a shift of the Fermi level can be achieved by applying a reverse bias across a p-n or Schottky barrier junction. In these conditions, in the vicinity of the junction a region with near intrinsic Si properties is set up where the Fermi level is effectively in the middle of the Si band gap.

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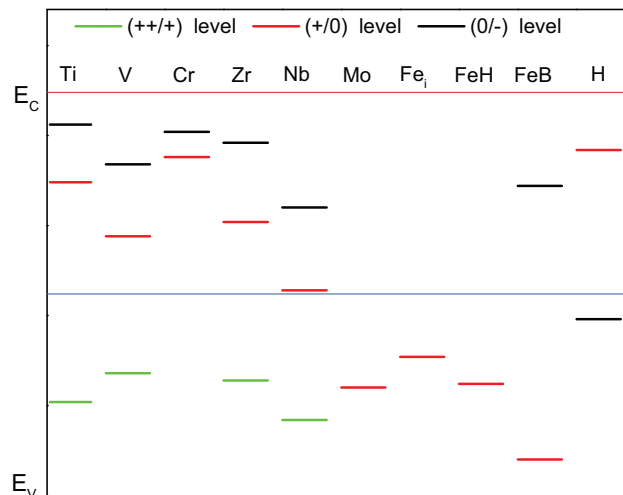


Figure 1. Graphical representation of the electrically active levels of a range of transition metals and hydrogen in the silicon band gap. The conduction and valence band edges are denoted E_c and E_v , respectively, the line at mid-gap represents the idealized Fermi level in intrinsic material.

In p-type material if an energy level of a given defect lies in the lower half of the band gap in the intrinsic region the defect will undergo a change in charge state. If the $(0/+)$ energy level is in the lower half of the band gap, the defect will become neutrally charged, and so is able to bond with hydrogen, which is seen to remain positively charged during annealing under reverse bias^[11,20] and expected to remain in the positive charge state as long as the Fermi level remains below $\approx E_c - 0.4$ eV.^[25] This behavior is due to the negative-U nature of the hydrogen atom in Si for which the donor state is above the acceptor state and as a consequence the neutral state is unstable in equilibrium.^[25] The formation of metal-hydrogen complexes in p-type Si during anneals under reverse bias has previously been reported, for example in the case of Fe,^[8,20] Co,^[14] and Ag,^[16] the TMs with the $(0/+)$ level in the lower half of the silicon band gap.

An alternative means of changing the charge states of defects in silicon is through the introduction of significant concentrations of minority carriers. This, in principle, can facilitate interactions between similarly charged TMs and H through reactions of the form $TM^+ + e^- + H^+ \leftrightarrow [TM-H]$. Illuminated annealing of hydrogenated Si samples has previously been shown to be able to increase carrier lifetime in p-type multicrystalline silicon,^[26] and is predicted to be due to enhanced hydrogen passivation of defects in the material following manipulation of the charge state of hydrogen in the material.^[27,28]

The probability of a defect to be in a particular charge state under the injection of minority carriers can be modeled in detail, and depends on both the excess concentration of charge carriers and the capture and emission rates of electrons and holes for a given defect. The behavior of two transition metals, Fe and Cr, as well as hydrogen in p-type Si has recently been modelled in Ref. [29] for various injection conditions, in which the relative concentration of positively charged and neutral interstitial TM atoms (e.g., $[Fe_i^+]/[Fe_i^0]$) is predicted to change significantly for different injection levels.

In this paper, we present a study of the interactions of one of the slowest diffusing TMs – molybdenum, with hydrogen in p-

type silicon. DLTS measurements have previously been used to show that interstitial Mo (Mo_i) presents one level in the Si band gap at $E_v + 0.30$ eV,^[30–32] predicted to be due to the Mo_i related $(0/+)$ charge state transition.^[33] As such Mo-H bonding in p-type silicon can occur in near-intrinsic conditions. The formation of Mo-H complexes in p-type Si has been evidenced in our work by electrical measurements following annealing of the samples first under the application of a reverse bias, as well as through the introduction of a significant flux of minority carriers under illumination with an 850 nm light emitting diode (LED).

2. Experimental Section

In this work, we have used electrical measurements [deep level transient spectroscopy (DLTS), Laplace DLTS (LDLTS) and capacitance and current–voltage (C–V/I–V) measurements] to investigate the electrically active interstitial molybdenum and its interactions with hydrogen in p-type silicon.

Epitaxially grown p-type silicon wafers doped with boron to $[B_s] \approx 2 \times 10^{15} \text{ cm}^{-3}$ and contaminated with different concentrations of molybdenum during growth have been studied. The maximum Mo concentration was $\approx 4 \times 10^{13} \text{ cm}^{-3}$. Slices from the wafers were treated with a 50 W remote hydrogen plasma at room temperature in order to introduce significant quantities of hydrogen. After hydrogenation, small samples were cut from the slices and processed immediately after hydrogenation, or following annealing with or without illumination.

Illuminated annealing was carried out at 200°C under light generated by an 850 nm LED with a measured output power of ≈ 100 mW for 30 min, after which samples were cooled to room temperature under illumination for a further 30 min. Control samples were annealed in the same conditions with no illumination. After annealing with or without illumination, samples were prepared for electrical measurement (DLTS, LDLTS, and CV–IV).

Schottky barrier diodes (SBD's) of diameter 1 mm were formed on the surface of the samples by plasma sputtering of Ti

and Al, and an Ohmic contact was formed on the back surface of the samples by thermal evaporation of Au. The quality of the diodes was tested using CV and IV measurements, which also provided the concentration of shallow acceptors and the probing depth achievable in DLTS measurements.

DLTS and LDLS measurements were undertaken on samples following hydrogenation, as well as after thermal treatment with or without illumination. In addition, plasma treated samples were studied following reverse bias annealing (RBA). In this process, the samples were annealed at 110 °C under a reverse bias of 7 V for 30 min. This treatment has two main effects; firstly, hydrogen is redistributed within the sample, moving away from the sample surface. Secondly, the depletion region is extended in the material for the duration of the reverse bias anneal. Finally, the samples were studied after annealing at temperatures up to 250 °C in the dark in order to observe the stability of any Mo-H complexes formed.

3. Results and Discussion

3.1. Presence of Molybdenum in Hydrogen Plasma Treated Samples

Conventional DLTS spectra recorded on hydrogen plasma treated epitaxially grown p-type silicon with and without molybdenum contamination are shown in Figure 2. One clear peak with its maximum at around 170 K is present in the DLTS spectrum of the sample contaminated with molybdenum. This peak is marked as H_1 in Figure 2. The activation energy for hole emission for the trap responsible for this peak was determined using an Arrhenius plot of T^2 -corrected hole emission rates to be 0.30 eV from the valence band edge.

This value is in good agreement with the previously determined hole emission energies for interstitial molybdenum (Mo_i) in silicon^[11,30,31] and so this peak is assigned to the (0/+) level of Mo_i , with the average concentration $[Mo_i] \approx 4 \times 10^{13} \text{ cm}^{-3}$ in the probed region.

3.2. Effect of Reverse Bias Annealing on Interstitial Molybdenum Concentration

Having confirmed the presence of molybdenum in the samples used in this study and estimated its concentration in the plasma treated material, the samples were studied following reverse bias annealing (RBA). This treatment extended the depletion region further into the silicon, shifting the Fermi level to the mid gap. In this region, molybdenum transformed from the positive to the neutral charge state (see the position of the (0/+) level of Mo_i in Figure 1) in which it was able to interact with positively charged hydrogen.

The result of this process is displayed in Figure 3, which shows the normalized conventional DLTS spectra for the H plasma treated epi-p-Si:Mo samples before and after reverse bias annealing, as well as after a further 30 min anneal at 250 °C.

It can be seen in Figure 3 that after reverse bias annealing, the apparent concentration of interstitial molybdenum has been reduced significantly, with no additional peaks observed in the DLTS spectra, so indicating the formation of Mo-H complexes with no deep levels in the lower part of the band gap. When the sample is annealed at 250 °C, a temperature known to dissociate previously studied transition-metal-hydrogen complexes in n-type silicon,^[8,9] a partial recovery of the interstitial molybdenum concentration is observed, supporting the suggestion of the formation of Mo-H complexes upon reverse bias annealing.

The concentration of interstitial molybdenum versus depth from the sample surface (W) was also measured before and after reverse bias annealing, as well as after annealing at 250 °C using Laplace DLTS and the resulting concentration-depth profiles are shown in Figure 4a. In Figure 4b these are compared to the concentrations of uncompensated shallow acceptors (N_A) determined from capacitance-voltage measurements.

The effect of reverse bias annealing on the concentration of shallow acceptors is immediately apparent in Figure 4b. The dip in the $N_A(W)$ curve after the reverse bias annealing indicate that B-H-pairs, which were formed in the sub-surface regions of the

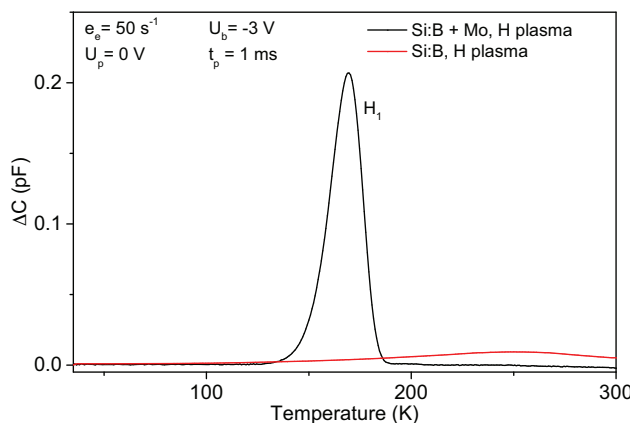


Figure 2. DLTS spectra of epitaxially grown silicon with and without molybdenum contamination following hydrogen plasma treatment. Measurement settings [DLTS rate window (e_0), bias voltage (U_b), filling pulse voltage (U_p), and filling pulse length (t_p)] are shown on the graph.

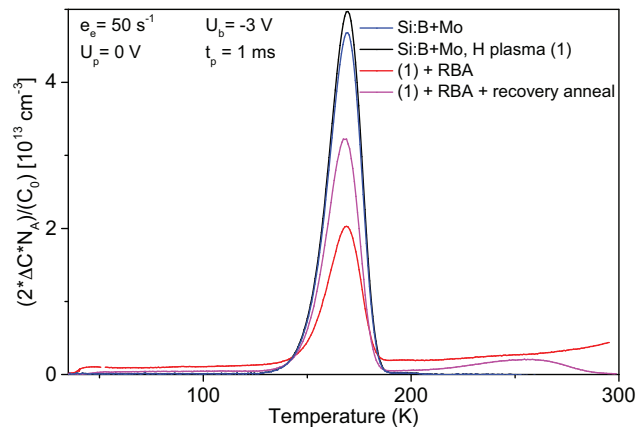


Figure 3. DLTS spectra of epi-p-Si:Mo after hydrogen plasma treatment, following a 30 min anneal under +7 V reverse bias at 110 °C (denoted RBA), and after a 30 min anneal at 250 °C. Measurement settings are shown on the graph.

samples during H plasma exposure, were dissociated upon RBA. Positively charged hydrogen atoms were then able to drift away from the surface in the electric field of the Schottky diode and interact with boron atoms in deeper regions. The highest concentration of the B-H pairs occurred between 3 and 4 microns from the sample surface after the RBA treatment.

Comparing this to the concentration-depth profile for Mo_i , we see that following reverse bias annealing, the concentration of Mo_i is reduced throughout the region probed by LDITS, as suggested by the conventional DLTS measurements presented in Figure 3. The concentration of electrically active Mo_i is also seen to be significantly reduced in the region in which the hydrogen concentration is likely to be greatest, further suggesting the formation of Mo-H complexes with no levels in the lower half of the band gap during reverse bias annealing.

Following a recovery anneal at 250 °C, it can be seen that the Mo_i concentration partially recovers, so indicating that the binding energy of any electrically inactive Mo-H complexes

formed is low, and comparable to those for previously observed TM-H complexes in n-type Si, ≤ 2 eV.^[11,18,20,22]

3.3. Effect of Illuminated Annealing on Interstitial Molybdenum Concentration

Having demonstrated that shifting the Fermi level to the middle of the silicon band gap using an applied reverse bias allows the formation of electrically inactive Mo-H complexes, and suggesting a change in charge state of interstitial Mo atoms, the possibility of similar interactions mediated by a flux of minority carriers was studied.

DLTS spectra were recorded on samples of epi-p-Si:Mo after hydrogen plasma treatment, as well as following annealing at 200 °C for 30 min with or without illumination using an 850 nm LED with output power ≈ 100 mW focused on an area of 5×5 mm. After annealing, samples were cooled to room

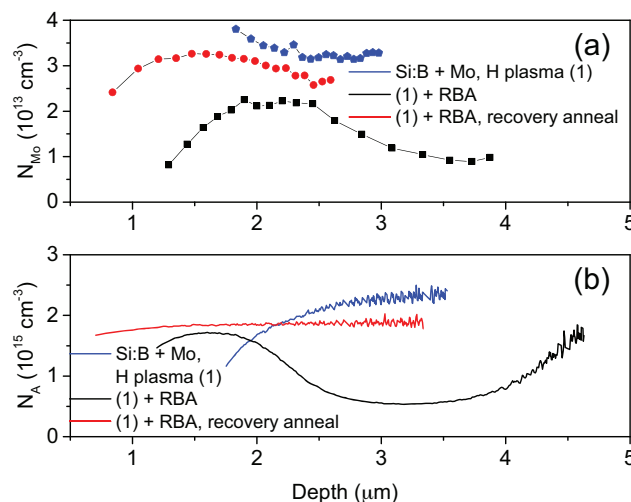


Figure 4. Concentration-depth profiles of interstitial Mo (a) and shallow acceptor concentration (b) in epi-p-Si:Mo after hydrogen plasma treatment, following a 30 min anneal under +7 V reverse bias (denoted RBA) at 110 °C, and after a 30 min anneal at 250 °C.

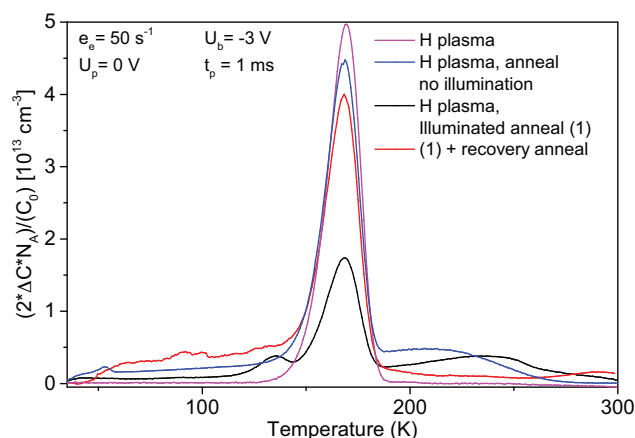


Figure 5. DLTS spectra of epi-p-Si:Mo after hydrogen plasma treatment, following a 30 min anneal at 200 °C with or without illumination at 850 nm, and after a 30 min anneal at 250 °C in the dark. Measurement settings are shown on the graph.

temperature for a further 30 min, with illumination continued during cooling of the illuminated samples. The photon flux achieved during this process was estimated to be $\approx 1.8 \times 10^{18} \text{ cm}^{-2}$, comparable to that used in previous studies in which illuminated annealing was shown to result in some increase in minority carrier lifetime.^[28] The measured DLTS spectra are shown in **Figure 5**.

It can be seen in **Figure 5** that the estimated concentration of interstitial Mo is significantly lower in the sample annealed under illumination than in that subjected to only hydrogen plasma treatment. A small peak with its maximum at about 130 K is also seen to appear in the DLTS spectrum of the sample annealed under illumination, which could be due to an energy level of a molybdenum-hydrogen complex formed during illuminated annealing.

Annealing under the same conditions without illumination can be seen not to result in a similar reduction in the concentration of Mo_i. When samples, in which the electrically

active molybdenum concentration was reduced, are further annealed at 250 °C, a recovery in the Mo_i concentration is seen to occur, similar to that observed in samples subjected to reverse bias annealing (**Figure 3**). This suggests that annealing under illumination is able to influence the charge state of Mo or H and permit the formation of Mo-H complexes in p-type Si. It is possible to estimate relative concentrations of Mo and H atoms in different charge states under illumination conditions in Si crystals by calculations similar to those done in Ref. [29]. It should be mentioned, however, that the results of such estimation will not be very reliable as several defect parameters needed for such calculations are unknown. Particularly, there are no reliable data on the capture cross section of electrons and holes by hydrogen atoms in different charge states. Our rough estimation of the relative concentration of hydrogen atoms in different charge states using the data from Ref. [29] indicates that the majority of H atoms should be in the positive charge state in the material under the illumination conditions used. So, it is

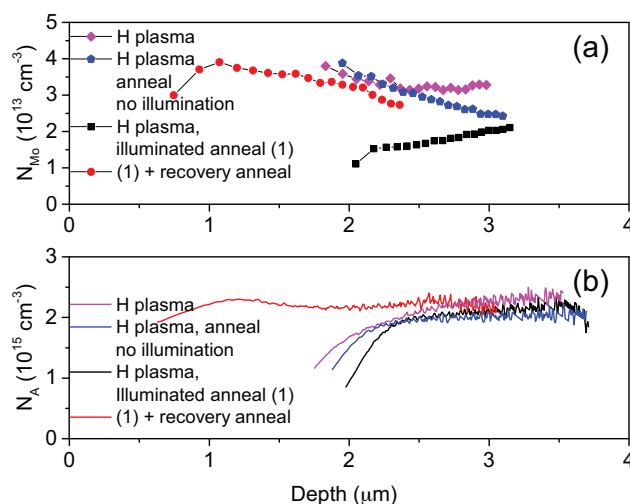


Figure 6. Concentration-depth profiles of interstitial Mo (a) and shallow acceptor concentration (b) in epi-p-Si:Mo after hydrogen plasma treatment, following a 30 min anneal at 200 °C with and without illumination at 850 nm, and after a 30 min anneal at 250 °C in the dark.

likely the illumination-induced formation of Mo-H complexes observed in our work is related to the interaction of positively charged hydrogen with neutral Mo atoms.

The concentration of interstitial molybdenum versus depth from the sample surface was also measured in samples subjected to annealing treatments with and without illumination, as well as after annealing at 250 °C using Laplace DLTS and the resulting concentration-depth profiles are shown in **Figure 6a**. This is compared to the concentration of shallow acceptors determined from capacitance-voltage measurements in **Figure 6b**.

In **Figure 6b**, the concentration of shallow acceptors can be seen to remain practically unchanged following annealing with or without illumination when compared to samples after hydrogen plasma treatment. The concentration of interstitial Mo, however, is reduced by about 50% in the sample subjected to illuminated annealing, as suggested from conventional DLTS measurements shown in **Figure 5**. Similar reductions are not seen to occur in the sample annealed without illumination.

Subsequent annealing of the illuminated samples at 250 °C for 30 min is seen to result in a recovery of the electrically active Mo_i concentration, as observed for the samples subjected to reverse bias annealing (**Figure 3a**). This suggests that the reduction in Mo_i concentration following illuminated annealing is likely due to the formation of electrically inactive Mo-H complexes which can dissociate upon annealing at 250 °C.

4. Conclusions

In this paper, we have studied the formation of molybdenum-hydrogen complexes in p-type silicon contaminated with Mo. We have shown that under equilibrium conditions, no signals from Mo-H complexes are observed in the DLTS spectra, and attribute this to the Coulombic repulsion of the positively charged atoms of interstitial molybdenum and hydrogen in p-type Si.

Shifting the Fermi level to the middle of the band gap by applying a reverse bias across a Schottky junction during annealing at 110 °C is shown to redistribute hydrogen, and reduce the observed concentration of electrically active Mo_i atoms, with greater reductions in regions with the highest concentration of hydrogen. This reduction is shown to be partially reversible following annealing at 250 °C, and it is suggested that the observed reduction is due to the formation of electrically inactive Mo-H complexes during reverse bias annealing.

Annealing under illumination at 850 nm is shown to result in similar reductions in the electrically active Mo_i concentration, with control annealing treatments without illumination shown to have no effect. As with the reverse bias annealed samples, further annealing at 250 °C recovers the initial Mo_i concentration, suggesting that Mo-H bonding occurs during illuminated annealing of p-type Si. The results obtained show that illuminated annealing of hydrogenated p-type Si could provide a means of reducing the concentration of electrically active Mo in solar Si, and hence can suppress its effect on carrier lifetime. Our preliminary results on illuminated annealing of hydrogenated Si crystals contaminated with titanium and vanadium indicate that illuminated annealing could also be an effective method of

reducing the recombination activity of other common transition metals in silicon.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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