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in, and J. H. Tucker, irray, A. Tipping and . R. Huff and K. G. PASSIVATION OF SHALLOW ACCEPTORS IN SI AND GAAS BY ANNEALING IN H2

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ABSTRACT

In this paper we describe two examples of the passivation of shallow acceptors in semiconductors by annealing in $\rm H_2$ gas. In the first, a fraction of the shallow acceptors are shown to be passivated throughout the bulk of a Si sample that is several mm thick by annealing in $\rm H_2$ gas at 1280°C and quenching. In the second, epitaxial GaAs:C grown by metalorganic MBE or MOCVD is shown to be partially passivated near 500°C by $\rm H_2$ gas that is either in annealing or growth ambients.

I. INTRODUCTION

Most recent work on H in semiconductors [1-3] has focussed on defect passivation in a plasma that contains atomic hydrogen. In the following sections we discuss two new examples where H₂ in growth or annealing ambients leads to significant H incorporation and shallow impurity-H complex formation. (i) Acceptors in Si can by passivated by annealing in H₂ at elevated temperatures (900°C-1280°C) and then quenching rapidly. [4-6] (ii) In GaAs:C epitaxial layers grown by metalorganic MBE (MOMBE) or MOCVD, we have found that annealing in H₂ at 500°C leads to a substantial partial passivation of the C in the layer. Typical growth temperatures and processing-related annealing steps are performed near 500°C; H₂ gas in growth or processing ambients is shown to lead to C-H complex formation.

Although H-passivation from H-containing plasmas has dominated recent work, there are a number of cases where H₂ in growth and annealing ambients has been shown to lead to H incorporation and/or defect passivation. In elemental hosts, Hall [7] and Haller and coworkers [8] have discovered several H-related species in Ge that had been grown in H₂. Si grown in an H₂ atmosphere is also known to contain a number of H-related defects.[9] In experiments performed by the Sievers group,[10,11] annealing Si in H₂ gas led to the formation of impurity-H complexes.

In III-V and II-VI host materials, there are a few examples of H incorporation from $\rm H_2$ gas of which we are aware. Svob and coworkers diffused D into GaAs [12] and II-VI materials [13] from D₂ gas and detected the D with SIMS. In more recent work, Svob et al. [14] showed with SIMS measurements that H was incorporated into II-VI materials grown by MOCVD from $\rm H_2$ in the growth ambient. Defect passivation was not demonstrated in these experiments.

Here we focus on the passivation of shallow impurities by hydrogen following growth or annealing in an $\rm H_2$ containing ambient. In our studies, IR absorption due to H-stretching vibrations is the primary probe of the passivated shallow impurities.

II. PASSIVATION OF SHALLOW ACCEPTORS IN Si

In our experiments, Si samples were sealed in quartz ampules that had been evacuated and then filled with 0.6 atm of $\rm H_2$ gas at room temperature. The sealed ampules were annealed at temperatures between

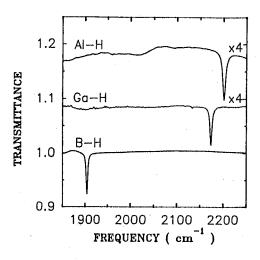


Fig. 1. IR spectra measured near liquid He temperature for acceptor-doped, Si samples that had been annealed in H₂ gas at 1280°C for 30 min. and then quenched to room temperature. The acceptor concentrations are 6x10¹⁶ 1x10¹⁶, and 0.7x10¹⁶ cm⁻³ for the B, Al, and Ga doped samples, respectively.

900°C and 1280°C and then quenched to room temperature by withdrawing the ampule from the furnace and dropping it into ethylene qlycol at room temperature. IR absorption spectra were measured at a resolution of 2 cm $^{-1}$ with a Bomem DA3.16 Fourier transform spectrometer.

IR spectra of bulk, acceptor-doped Si samples (with N_A of the order of $10^{16}~\rm cm^{-3}$) that had been annealed in H₂ are shown in Fig. 1. The H-stretching features have frequencies and absorption strengths similar to those reported for acceptor-H complexes in samples that were doped with concentrations greater that $10^{18}\rm cm^{-3}$ by ion-implantation and then passivated by exposure to a hydrogen plasma.[15] Absorption strengths in the H₂-soaked, uniformly doped samples that are comparable to thin, heavily doped layers implies acceptor passivation well into the bulk of the H₂-soaked samples. To confirm that the passivation was uniform throughout the sample thickness, we remeasured the IR absorption after grinding 1 mm from the surfaces of an H₂ treated, B-doped sample that was initially 3 mm thick. Vibrational absorption due to B-H centers was observed with a strength consistent with the 1 mm thickness of the thinned sample and a uniform distribution of centers throughout the sample.

To determine [B-H] from the strength of the IR absorption at 1903 cm $^{-1}$ we have reexamined previous results [16] for a B-implanted sample that had been passivated in an H $_2$ plasma. The calibration is given by, $[B-H]/A = 2.5 \times 10^{15} \text{ cm}^{-1}. \tag{1}$

This calibration is close to that determined for Al-H complexes in Si [15] and also to a recent calibration of the B-H absorption by McQuaid et al. [5] With the calibration given by Eq. (1) we find that [B-H] = $4.6x10^{15}$ and $5.0x10^{14}$ cm⁻³ for samples with [B] = $1.7x10^{17}$ and $1.6x10^{16}$ cm⁻³, respectively. Hence, approximately 3% of the B is passivated by the anneal in $^{\rm H}_2$ at 1280°C. For the Al doped sample we find [Al-H]= $1.3x10^{15}$ cm⁻³ and that 8% of the Al is passivated. The more complete passivation of Al is consistent with this complex's greater binding energy. [17]

We have explored the role of the temperature and duration of the $\rm H_2$ -soaking treatment on the concentration of B-H complexes that are formed. In Fig. 2 are plotted the concentrations of B-H complexes vs. the reciprocal of the temperature of the $\rm H_2$ anneal for the samples doped with [B] = 1.7×10^{17} cm⁻³. The open circles are for 30 min. anneals and the closed squares are for 120 min anneals. At 1100°C,

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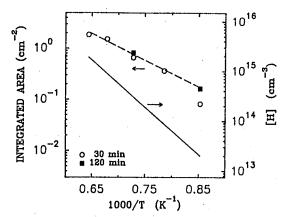


Fig. 2. The integrated absorption coefficient, A, for the H-stretching vibration of the B-H complex vs. the reciprocal of the annealing temperature for Si samples with [B] = 1.7x10¹⁷ cm⁻³ that were annealed in H₂, and then quenched. The concentration scale on the right is related to A by Eq.(1) in the text. The solid line is the solubility of H in pure Si determined by Van Wieringen and Warmoltz.

increasing the duration of the anneal increases the strength of B-H absorption only slightly. At 900°C, increasing the duration of the anneal increases the B-H absorption by roughly a factor of 2 indicating that H has not fully diffused through the sample during the 30 min anneal. The diffusion constant determined by Van Wieringen and Warmoltz (VWW) [18] is 3.7×10^{15} cm²/s at 900°C which gives a \sqrt{D} C diffusion length of 0.26 cm for the 30 min anneal in H₂ which is comparable to the thickness of the sample.

The dashed line shown in Fig. 2 is the best fit to the data. (At 900° C, the data for the 120 min anneal was used.) If we use the calibration of the B-H absorption given in Eq. (1), the dependence of [B-H] upon annealing temperature for our samples is given by

$$[B-H] = 1.2 \times 10^{19} \exp(-1.04 \text{eV/kT}) \text{ cm}^{-3}$$
 (2)

Also shown in Fig. 2 is the hydrogen solubility determined by Van Wieringen and Warmoltz [18], $S_{\rm H}=2.4{\rm x}10^{21}~{\rm exp}(-1.88{\rm eV/kT})$ cm⁻³. While the B-H concentration is greater than the VWW value by only a factor of 2.7 at 1280°C, the B-H concentration in our samples annealed at 900°C exceeds the VWW value by a factor of 20. The activation energies in Eq.(2) and in the solubility determined by VWW differ by nearly a factor of 2.

When H was introduced into n-type Si doped with P or As in the mid-10¹⁶ cm⁻³ range by annealing at 1280°C in $\rm H_2$ gas and quenching, IR absorption bands at 1555 and 1561°cm⁻¹ that have been assigned to P-H and As-H complexes [15,19] were not detected. We conclude that shallow donors are not passivated as efficiently as acceptors by the introduction of H into our samples at high temperatures.

Previous studies of H-passivated shallow impurities are made possible, in part, by the high solubility of the dopant. To have a sufficient number of centers in the micron-thick, H-passivated layers that are typical of plasma exposed samples, the dopant concentration must be large. The study of hydrogen-passivated deep impurities has been hampered by their lower solubility which does not lead to a sufficient total number of hydrogen-passivated centers for easy examination by structure sensitive techniques such as IR absorption or EPR. Hence, we expect that there will be renewed interest in techniques by which H can be introduced throughout the bulk of a semiconductor sample. The total number of centers introduced should permit structure-sensitive studies of species with solubilities that are decades smaller than is typical of common dopants.

III. PASSIVATION OF GaAs: CAS GROWN BY MOMBE OR MOCVD

In our experiments on the passivation of GaAs:C, several epitaxial layers grown by MOMBE and MOCVD with various growth conditions were examined. MOMBE samples were grown in a Varian Gas-Source Gen II on semi-insulating GaAs substrates.[20] Most samples studied were grown from AsH3 and trimethylgallium (TMG) that was introduced with He carrier gas. The AsH3 was introduced through a low pressure cracker heated to 950°C. The growth temperature was 500°C. Immediately after the growth, the substrate heater was switched off and the sample was allowed to cool to 475°C which took 30 s. The AsH3 flow was stopped and the sample was unloaded. A few MOMBE samples were grown from TMG and a solid As source; for one of these samples a flow of H2 gas was introduced into the growth chamber.

MOCVD samples were grown from triethylgallium and trimethylarsine following the method of Kobayashi and Inoue.[21] The substrate temperature was 545°C. The metalorganic sources were introduced with hydrogen carrier gas.

Annealing experiments were performed either in an RTA oven with an ambient of forming gas or He or in a muffle furnace in sealed quartz ampules. Characterization methods include Hall effect, SIMS (Cs † beam with ion-implanted standards), and IR absorption.

IR spectra for the H-stretching region are shown in Fig. 3 for samples from a MOMBE-grown layer with $\rm N_A=9.4 \times 10^{19}~cm^{-3}$ that had been annealed in various ambients. In Fig. 3(a) a feature at 2635 cm⁻¹ that was previously assigned to the C_{As}-H center by Clerjaud et al. [22] and additional features at 2643, 2651, and 2688 cm⁻¹ that also involve C and H [23] are seen in an as-grown layer. We use the denotation $\rm C_X$ -H for these centers.

In previous work it was found that H could be introduced into the GaAs:C layers grown by MOMBE from the TMG or the AsH $_3$ sources. [23,24] Fig. 3 shows that H $_2$ in the annealing ambient is also an important source of H in the layers. The spectrum in Fig. 3(b) shows that annealing in H $_2$ enhances the strength of the C-H stretching feature at 2635 cm $^{-1}$. This anneal was performed in a sealed ampule; spurious sources of atomic H that might result from the dissociation of H $_2$ on hot furnace components are unlikely. In Figs.

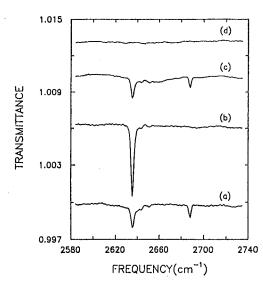


Fig. 3. IR spectra that demonstrate the effect of annealing ambient on C-H centers in GaAs:C grown by MOMBE. Samples were selected from the same wafer with $N_A=9.4\times10^{19}\,\mathrm{cm}^{-3}$. (a) Asgrown. (b) Anneal at 450°C in 0.6 atm H_2 in a sealed ampoule. (c) Anneal for 5 min in forming gas at 600°C in an RTA oven. (d) Anneal for 5 min in He at 600°C in an RTA oven.

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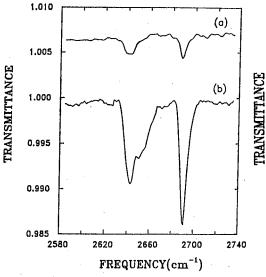
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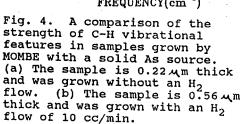
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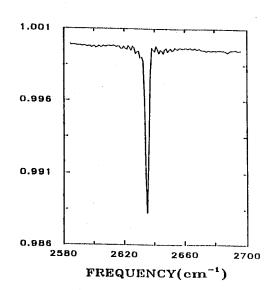


Fig. 5. IR spectrum measured near liquid He temperature for an as-grown GaAs:C layer grown by MocVD. $N_A = 2 \times 10^{19}$ cm⁻³.

3(c) and (d), samples are compared following annealing in an RTA oven in forming gas (90% N $_2$ and 10% H $_2$) and He gas. An anneal in the inert He ambient at 600°C eliminates the C $_{\rm X}$ -H centers whereas, following an anneal at 600°C in forming gas, C $_{\rm X}$ -H centers remain.

To confirm that $\rm H_2$ present during growth can passivate C acceptors in GaAs:C, we have compared two epilayers grown from TMG and a solid As source. For one epilayer a flow of $\rm H_2$ (10 cc/min) was introduced into the MOMBE growth chamber. IR spectra of these samples are shown in Figs 4(a) and (b). C-H centers are present in the layer grown from the TMG source and solid As indicating that the TMG alone is a source of H in the layer. Introducing $\rm H_2$ gas into the chamber enhances the C-H-related IR absorption and hence the concentration of passivated C in the layer. When one accounts for the different layer thicknesses, it is found that the hydrogen content is increased by 2.7 times for the sample grown in an $\rm H_2$ flow.

An IR spectrum is shown in Fig. 5 for an as-grown, GaAs:C layer grown by MOCVD. The strong feature at 2635 cm $^{-1}$ assigned to $\rm C_{AS}-H$ centers is present. The metalorganic sources and $\rm H_2$ carrier gas are the likely sources of H in the epilayer.

The presence of C_X -H centers in as-grown samples indicates that these defects are stable near the epi-growth temperature. Isochronal (5 min) annealing data are shown in Fig. 6. These anneals were performed in an RTA furnace in a He ambient. The 2635 and 2688 cm⁻¹ features are annealed away at temperatures of 800 K (527°C) and 900 K (627°C), respectively. Both centers are stable or marginally stable at the epi-growth temperatures of 500 and 545°C for the MOMBE and MOCVD growths, respectively, and persist to higher temperatures when samples are annealed in H₂-containing ambients. [See Fig. 3(c)].

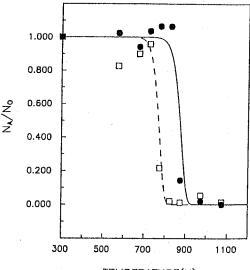


Fig. 6. Isochronal annealing data for the 2636 cm $^{-1}$ (open squares) and 2688 cm $^{-1}$ (closed circles) absorption signals in epitaxial GaAs:C grown by MOMBE. Anneals were performed for 5 min in a He ambient. Here, $N_A = 2 \times 10^{20}$ cm $^{-3}$.

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The stability of the $C_{\rm AS}$ -H center (2635 cm⁻¹) is consistent with previous results reported by Clerjaud et al. [25]

We have made an approximate calibration of the concentration of centers that include C and H by making a direct measurement of the H concentration with SIMS. It was assumed that all of the hydrogen in the layers was involved in stable C_{χ} -H complexes and that the different C-H stretching features have the same calibration factor. With these approximations the calibration is

$$[C_X-H]/A = 1.8 \times 10^{16} \text{ cm}^{-1}$$
 (3)

Here [C_X-H] refers to the total concentration of C_X-H centers and A is the integrated absorption coefficient, A = $\int \alpha (\sigma) d \Phi$, in units cm⁻² for the total H-stretching absorption due to the C_X-H centers.

With the calibration factor given in Eq.(3) we can estimate the concentrations of C_x -H centers in the various epilayers from the strength of the infrared absorption. The as-grown MOMBE layer in Fig. 3(a) has $[C_x-H]=7x10^{18}$ cm⁻³. Annealing in H_2 [Fig. 3(b)] increases the concentration of passivated carbon to $[C_x-H]=1.2x10^{19}$ cm⁻³ or to roughly 11% of the total [C]. The highest concentrations of C_x -H centers were observed in layers with H_2 in the growth ambient. The sample grown by MOMBE in a flow of H_2 [Fig. 4(b)] has $[C_x-H]=6.9x10^{19}$ cm⁻³. The MOCVD-grown layer [Fig. 5] has $[C_x-H]=1.4x10^{19}$ cm⁻³. The fraction of passivated C acceptors varies from 6% to 40% of the total acceptor concentration depending upon the growth method and growth conditions.

IV. CONCLUSION

In recent work, acceptor impurities in Si have been passivated by annealing bulk samples in H₂ at high temperature and quenching.[4-6] H is incorporated at concentrations that are well above the solubility of H determined by Van Wieringen and Warmoltz.[18] Similar treatments did not result in the passivation of shallow donors in n-type Si. It is expected that this bulk passivation technique will prove useful in studies of H-passivated deep levels.

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For GaAs:C epitaxial layers, $\rm H_2$ gas in growth and annealing ambients has been shown to lead to the formation of $\rm C_X$ -H complexes. Up to 40% of the C acceptors are estimated to be passivated in some cases. We presume that the $\rm H_2$ dissociates at the sample surface and then diffuses into the epilayer where $\rm C_x$ -H centers are readily formed. The $\rm C_x$ -H centers have been shown to be stable or marginally stable at temperatures near 500°C. Hence, the unintentional passivation of C is especially likely because typical epitaxial growth and processing-related annealing steps are performed near 500°C and often in H2 containing ambients.

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