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TITANIUM IN SILICON AS A DEEP LEVEL IMPURITY

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Abstract—Titanium inserted in silicon by diffusion or during Czochralski ingot growth is electrically active to a concentration level of about $4\times10^{14}\,cm^{-3}$. Hall measurements after diffusion show conversion of lightly doped p type Si to n type due to a Ti donor level at $E_C-0.22\,eV$. In DLTS measurements of n^+p structures this level shows as an electron (minority carrier) trap at $E_C-0.26\,eV$ with an electron capture cross section of about $3\times10^{-15}\,cm^2$ at 300°K. The DLTS curves also reveal a hole trap in the p type material. The $e_p\,(300/T)^2$ activation plot gives the level as $E_V+0.29\,eV$. The hole capture cross section is about $1.7\times10^{-17}\,cm^2$ at 300°K and decreases with decreasing temperature and the corrected trap level becomes $E_V=0.26\,eV$. Ti in lightly doped (360 ohm-cm) n type material does not result in conversion to p type so this level is inferred also to be a donor.

A Ti electrically active concentration of about $1.35\times10^{13}\,cm^{-3}$ in p type ($N_A=3.35\times10^{15}\,cm^{-3}$) Si results in a minority carrier (electron) lifetime of 50 nsec at 300°K.

1. INTRODUCTION

For some time, evidence has been accumulating that Ti in Si is a deep level impurity capable of causing serious reduction of minority carrier lifetime[1–4].

Titanium is a possible contaminant in polycrystalline silicon solar cells or in single-crystal cells fabricated from "solar grade" material derived from metallurgical silicon (Hopkins *et al.*[4]). Chemical purification of silicon by redistillation of chlorosilanes to produce semiconductor quality material is expensive. Attention therefore is being given to less expensive processes that might upgrade impure metallurgical silicon to an intermediate level of quality to be known as solar grade silicon[5]. Typical analyses have been given of metallurgical grade silicon by McCormick *et al.*[6] and Bartels[7].

Although Ti is present only in a concentration about 0.05% and the segregation coefficient is mid 10^{-6}, enough Ti may be expected in crystals pulled from metallurgical grade silicon that there is concern about the possible effects on solar cell performance. Studies at Westinghouse Electric Corporation for the Department of Energy have involved the growth of crystals containing $\leq10^{14}\,cm^{-3}$ Ti atoms. From n^+p solar cells fabricated from such crystals it has been determined that Ti causes a severe reduction in efficiency[4].

The study of the energy levels of Ti in Si appears to be limited to the report of a donor level at $E_C-0.21$ to 0.25 eV for MOS capacitance measurements of Ti ion implanted samples[2, 3].

The present work shows that Ti is associated with two donor levels in Si and that the capture cross sections are about 10^{-15} and $10^{-17}\,cm^2$ at 300°K. Hall measurements, DLTS and lifetime measurements have been made.

2. SAMPLE PREPARATION

Ti doped samples were obtained either from diffusion of Ti or from slices of Czochralski ingots grown from a melt containing Ti. The measurement methods involved the fabrication of diodes and bridge-shaped bulk specimens for Hall measurements. Slices were lapped and polished and surface contamination was removed by solvent (trichloroethylene, acetone and methanol) cleaning and 18 megohm high purity water rinse and further cleaned by successive soaks in hot HNO_3, H_2O, HF, H_2O, Acetone, and H_2O. Organic and metallic contamination was next removed by 20 min soaks in hot hydrogen peroxide solution—H_2O: H_2O_2: NH_4OH (5 : 2 : 1); $H_2O:H_2O_2:HCl$ (6 : 2 : 1) (Kern and Puotinen[8]) and the slices were finally given an H_2O rinse and blown dry in zero grade (not oil pumped) nitrogen gas.

For photomasking purposes and to protect the polished surface from pitting, a layer of thermal oxide was grown in wet O_2 at 1100–1200°C for 1 hr. Approximately one micrometer of SiO_2 was achieved by this process. The SiO_2 was stripped off the back of the wafer with HF, and the slice cleaved into strips to fit the Spectrosil fused quartz ampule. The slices were recleaned in hydrogen peroxide solutions and those to be titanium-diffused received a 1.5–2.0 μm layer of 4–9s pure titanium by electron beam evaporation at $0.5\text{–}1.5\times10^{-6}$ torr. Extensive use was made of control specimens, non-metal diffused, to be sure that contamination effects were excluded in the processing. The composition of the evaporated layer was monitored by Auger spectroscopy with sputter etching of the film. Purities of the films were good, showing no Cu or Au peaks and only a very slight peak of O on the exposed surface. To watch for any effect of the SiO_2 layer, some specimens were also prepared without an oxidation process.

As soon as the slices were taken through the above process, they were sealed in hydrogen peroxide cleaned Spectrosil tubing under a partial pressure of Argon of

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about 0.2 atm for ≥1100°C diffusions, and high vacuum for <1100°C. Control specimens (without the metal layer) were also sealed in similarly cleaned Spectrosil. The ampules were inserted into the uniform temperature zone of a diffusion furnace for 24–48 hr to insure saturation. Ampules were removed to a water bath quench at the end of the diffusion cycle. The back of each sample was lapped to remove any metal alloys. For the Hall specimens the front (oxide) sides were also lapped to have similar roughness on both sides. For the diode samples, the back was prepared for ohmic back-contact fabrication.

The ohmic back contact to p-type silicon was an alloyed p^+ region formed by heating an evaporated Al film for 5 min to 600°C in a flow of forming gas (95% N_2–5% H_2). The ohmic back contact to n-type silicon was an alloyed n^+ region formed by heating an evaporated layer of Sb and Sn for 5 min to 450°C in a flow of forming gas. An electrodeless plated Ni layer was applied over the Sb–Sn surface to produce the back contact.

Devices for capacitance studies were prepared without metal-oxide overlap since the oxide capacitance leads to difficulties of interpretation. Large diode areas were used here, thus reducing contact bonding problems. For these diodes, the oxide was completely removed and the junctions were formed by evaporating 0.050 in. diameter dots through a metal mask. For capacitance studies on n-type Si, Schottky barriers were formed by gold evaporation with no subsequent heat treatment.

3. HALL MEASUREMENTS

Titanium is found to compensate the hole concentration in p-type lightly doped material, indicating donor level action. Figure 1 shows Hall data for 200 ohm-cm p-type Si after titanium has been diffused for 48 hr at 1200°C. The Hall coefficient is negative indicating that overcompensation has occurred and that electrons are the majority carriers. The slope of the line indicates a donor level at about $E_C - 0.22$ eV.

Similar studies with 360 ohm-cm n-type silicon do not show compensation effects, and so we may infer that Ti inserted by diffusion does not exhibit an acceptor level, or one in any significant concentration. From the relatively small decrease of Hall electron concentration as the temperature is decreased we may infer that if there is an acceptor in the bandgap it is closer to the conduction band edge than $E_C - 0.1$ eV. Figure 2 shows the Hall data obtained after 1100 and 1200°C diffusion for 60 and 48 hr respectively into 360 ohm-cm n-type Si ($N_{\text{shallow}} \sim 1 \times 10^{13}$ cm^{-3}).

From the data of Fig. 2, we may infer that the concentration of active Ti donors is slightly over 10^{14} cm^{-3} after the 1200°C diffusion and quench and about 3×10^{13} cm^{-3} after the 1100°C diffusion. However it is also seen that

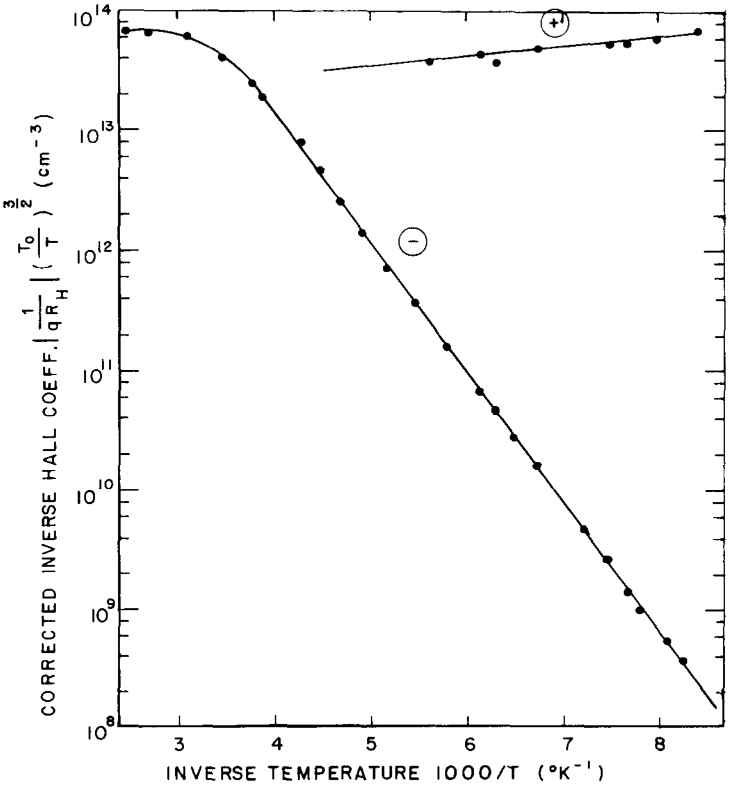

Fig. 1. Hall data showing the $E_C - 0.22$ eV donor level of Ti in 200 ohm-cm p-type silicon diffused at 1200°C for 48 hr to have an active titanium concentration of $\sim 2 \times 10^{14}$ cm^{-3}. The negative Hall coefficient indicates that electrons are the carriers. The control sample shows a positive coefficient with no concentration change over a wide temperature range.

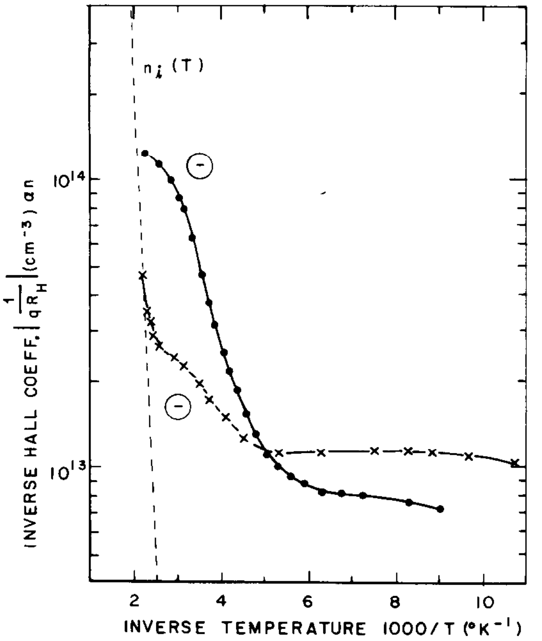

Fig. 2. Hall data showing the $E_C - 0.22$ eV donor level of Ti in 360 ohm-cm, *n*-type silicon diffused at 1200°C (●) for 48 hr and 1100°C for 60 hr (×) to have active titanium concentrations of 1.4×10^{14} and 2×10^{13} cm^{-3} respectively. The low temperature plateaus indicate the shallow (electron) carrier concentrations of the specimens.

the electron concentration from shallow donors at low temperatures is 1×10^{13} cm^{-3} after the 1100°C diffusion. Control specimens of the same material prepared identically and heated to these temperatures for 48 and 60 hr and quenched exhibited concentrations of about $1\text{–}2 \times 10^{13}$ cm^{-3} in agreement with that for unheated control specimens.

The $E_C - 0.22$ eV donor level inferred from Fig. 1 is in good agreement with the level $E_C - 0.21$ eV reported by Fahrner and Goetzberger[3] from surface capacitance studies after ion-implantation. The diffusion coefficient of Ti reported by Boldyrev *et al.*[9] is 10^{-11}–10^{-10} cm^2/sec for the temperature range of 1000–1250°C. Although we did not determine a diffusion coefficient the values of Boldyrev are compatible with our experience that tens of hours are needed at temperatures of 1100–1200°C to saturate slices of silicon of thickness about 3×10^{-2} cm.

The concentration of the Ti active center in silicon, inferred from our Hall studies, and DLTS studies as a function of the diffusion temperature is shown in Fig. 3.

4. DEEP LEVEL TRANSIENT SPECTROSCOPY STUDIES

DLTS studies of Schottky barrier and junction diode depletion region impurities were made by a fairly conventional 40 MHz DLTS circuit of the boxcar integrator kind pioneered by Lang[10, 11].

Typical DLTS response curves for Ti doped *n*-type Si (about 5 ohm-cm) are shown in Fig. 4. The DLTS response curves were made on Au-*n*-Si Schottky barrier junction specimens after 1000, 1100 and 1200°C Ti diffusions and quenches. The shallow doping concentrations were about 8×10^{14} cm^{-3} (phosphorus). Ti concentrations expected from the Hall measurements for similar diffusion conditions were 0.5×10^{13}, 2×10^{13} and 1.5×10^{14} cm^{-3} (Fig. 3). The voltage swing that controlled the depletion region thickness and initiated the transient was from -8 V to -2 V. The DLTS sampling times t_1 and t_2[10, 11] were usually in the range 0.01–10 msec and 0.09–90 msec. From such curves the electron emission coefficient of the Ti donor level was found to vary with temperature as shown in Fig. 5. The points on the lower half of the curve are derived from X–Y recorder traces of slow capacitance transients for two diodes observed with a 1 MHz Boonton capacitance meter type 72BD. They are seen to lie on the same line as the upper points which were derived from DLTS scans. This line with no correction applied for the variation of capture cross section with temperature represents a trap depth of $E_C - 0.26$ eV. The capture cross section at various temperatures was studied by the pulse width variation technique [10, 11] and no significant temperature variation was found (Fig. 6). Hence no correction for temperature is needed and 0.26 eV represents the final result. This is slightly larger than the $E_C - 0.22$ eV level observed by us from Hall measurements: the reason for the discrepancy was not established.

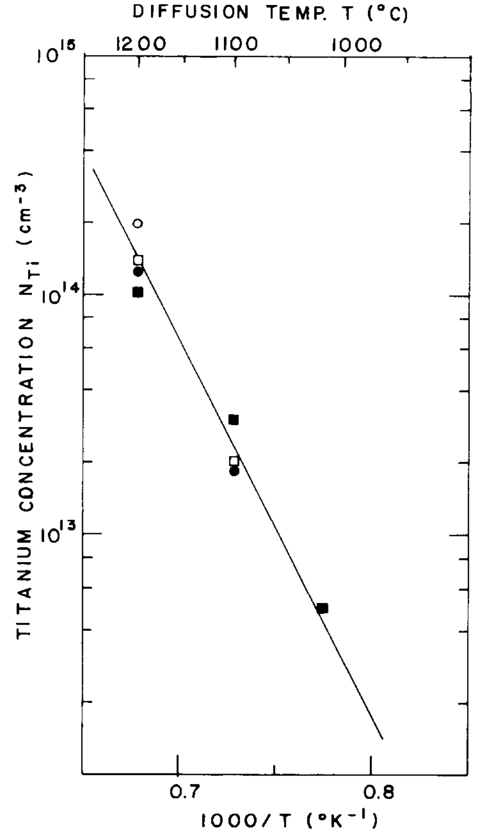

Fig. 3. Solubility of electrically active titanium vs diffusion temperature as inferred from Hall and DLTS measurements. Perhaps only about 20% of the Ti present is electrically active. Hall □ *n*-type, ○ *p*-type, DLTS ■ *n*-type, ● *p*-type. The *n*-type results are for the $E_c - 0.26(0.22)$ level and the *p*-type results for the $E_V + 0.26\,(0.29)$ eV level.

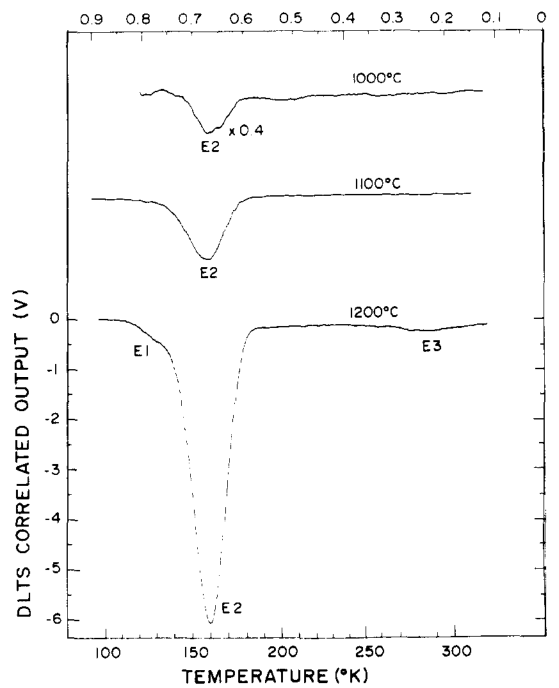

Fig. 4. Typical DLTS response curves for Au-nSi Schottky junction containing Ti with 1×10^{14}, 3×10^{13}, $5\times10^{12}\,\mathrm{cm}^{-3}$ for various diffusion temperatures. The initial voltage swing was from −8 V to −2 V with a 10 μsec pulse width. The t_1 and t_2 settings were 1 and 9 msec.

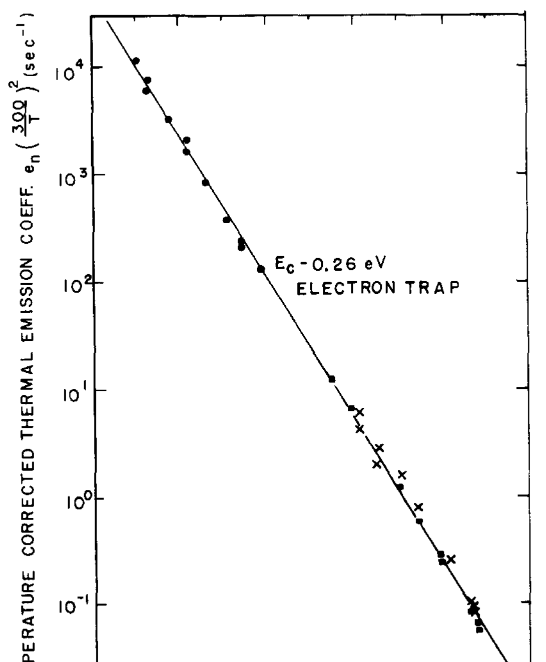

Fig. 5. Thermal emission data corrected for T^2 dependence of $N_C v_{th}$ for DLTS and capacitance transient measurements of 1200°C, 48 hr titanium diffused sample (5 ohm-cm n-Si) shown in Fig. 4.

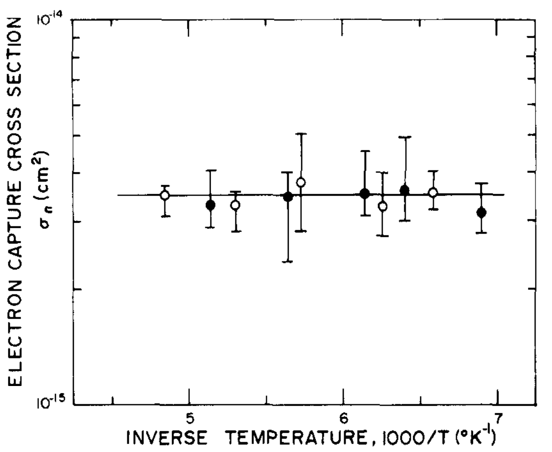

Fig. 6. The electron capture cross section at various temperatures was studied by the DLTS pulse width variation technique, for the titanium donor level at $E_C - 0.26$ eV shown in Figs. 4 and 5. No temperature dependence is observed.

The open circles are the data from 1200°C titanium diffusion and closed circles are the data from 1100°C titanium diffusion. The free carrier concentrations were measured by C^{-2} vs V_R and 4-point probe measurement to be 7.4×10^{14} and $9.5\times10^{14}\,\mathrm{cm}^{-3}$ respectively. The electron thermal velocity was taken as $1.14\times10^7\,(T/300)^{1/2}$ cm/sec.

The uncertainty bars represent the effects of the ±10 ns pulse width variation limitations of the HP 8013A pulse generator in the DLTS apparatus.

Some samples of Ti doped p type silicon, (by courtesy of Westinghouse R & D Center), in which the Ti was introduced during crystal pulling were also subjected to DLTS examination. The p-material contained $3.35\times10^{15}\,\mathrm{cm}^{-3}$ boron and the total Ti concentration (estimated from spark discharge mass spectroscopy and from neutron activation) was $2\times10^{14}\,\mathrm{cm}^{-3}$. The n^+p junction specimens were prepared by a $\mathrm{POCl_3}$ diffusion at 825°C for 50 min for a junction depth of about 0.3 μm. In this case $E_C - 0.26$ eV was seen as a minority (electron) carrier trap on the application of forward injection pulses. A majority (hole) carrier trap at $E_V + 0.29$ eV was also observed (Figs. 7 and 8). The electrically active concentration of the minority trap was estimated to be about $1.5\times10^{13}\,\mathrm{cm}^{-3}$ and the hole trap concentration was about $1.35\times10^{13}\,\mathrm{cm}^{-3}$.

Figure 9 shows a study of the hole capture cross section of the $E_V + 0.29$ eV level by the pulse width variation technique. The capture cross section was inferred to be $1\times10^{-17}\,\mathrm{cm}^2$. This capture cross section was found to increase with temperatures as $\sigma \propto \sigma_\infty \exp(-E_\infty/kT)$. Since the emission rate equation is

$$e = \frac{\sigma < v > N}{g} \exp(-E_T/kT)$$

it gives an apparent trap depth that is $E_T + E_\infty$. Here the temperature dependence observed results in a correction of the apparent hole trap level from 0.29 to about $E_V + 0.255$ eV.

In certain of our specimens that had the Ti inserted by diffusion and quenching with thermal oxide not grown on the front surface we observed the development of other

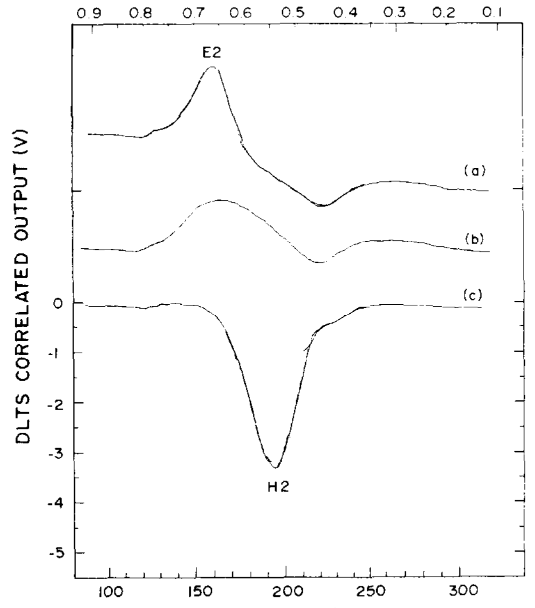

Fig. 7. DLTS spectra of the Czochralski grown, titanium doped p–Si ingot material n^+p junction diode was used and reverse biased at −6 V. (a) forward injection pulse from −6 V to +2 V, $E2$ ($E_C - 0.26\,\mathrm{eV}$) is observed as a minority trap, (b) forward injection pulse from −6 V to +1 V, $E2$ does not totally appear due to the majority trap $H2$ distortion, (c) voltage bias swing from −6 V to −1 V, hole trap $H2$ ($E_V + 0.29\,\mathrm{eV}$) is observed. Pulse width was 100 μsec in all cases. The rate window is $t_1/t_2 =$ 1.0/9.0 msec.

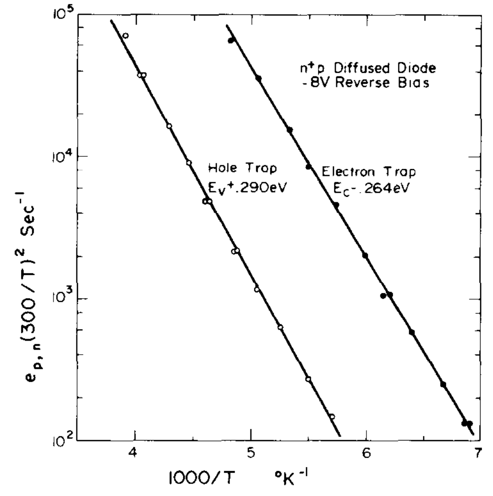

Fig. 8. Thermal emission coefficients for hole and electron traps observed in p type Si doped with about 3.6×10^{14} Ti cm^{-3} shown in Fig. 7.

defect levels. Figure 10 shows hole traps $H1$ and $H3$ that are developed in both the pSi Ti doped and the control specimens after a 1200°C heat cycle and quenching. These levels were found from Fig. 11 to be at energy levels (uncorrected) of $E_V + 0.33\,\mathrm{eV}$ and $E_V + 0.55\,\mathrm{eV}$. The hole capture cross section dependence on temperature of $H1$ and $H3$ are seen from Fig. 12 to be temperature independent in the limited range of the study. This figure also shows the capture cross section of an electron trap $E3$ found at $E_C - 0.55\,\mathrm{eV}$ in n type Si after a 1100°C Ti diffusion and quench.

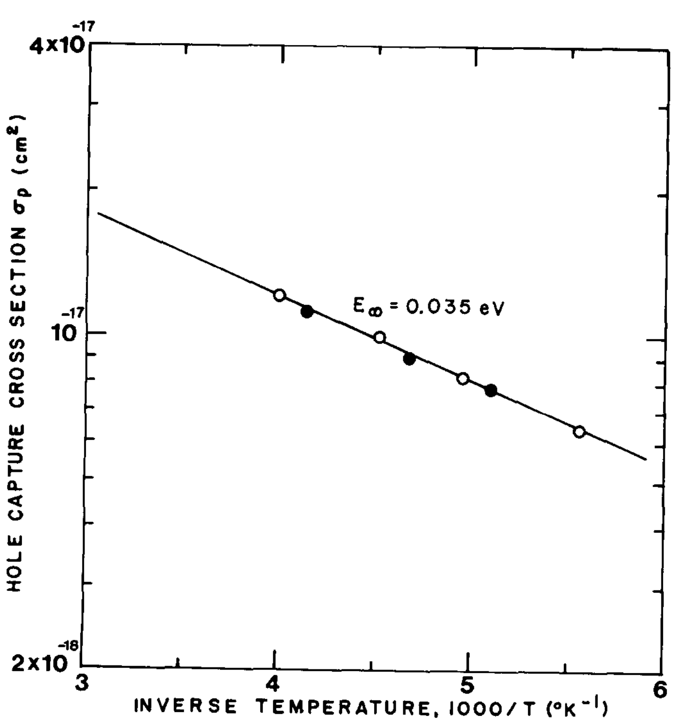

Fig. 9. Variation of hole capture cross section with temperature for p-Si:Ti (Westinghouse specimen). This temperature dependence leads to a trap level $E_V + 0.29 - 9.935\,\mathrm{eV} = E_V + 0.255\,\mathrm{eV}$. Al-$p$-Si Schottky diode by open circles, n^+p diffused diode by closed circles.

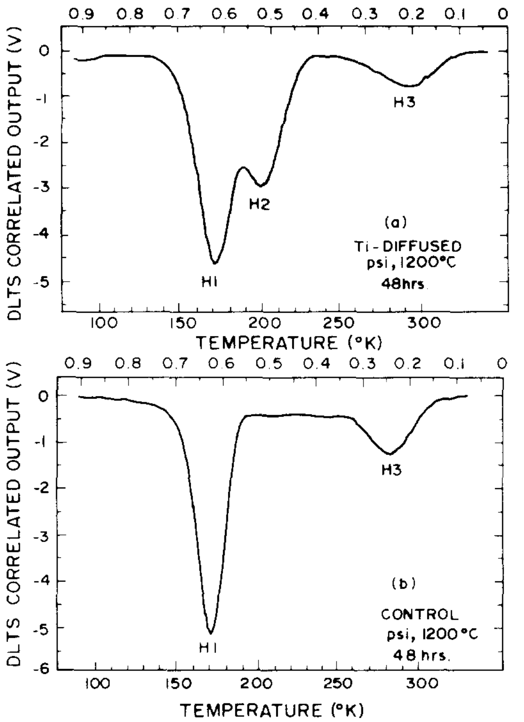

Fig. 10. DLTS spectra of the titanium-doped, p-Si material by ampoule diffusion at 1200°C. Specimens were prepared without thermal oxide protection on the front surface. Two defect levels in addition to Ti-related level $H2$ ($E_V + 0.30$ eV) were also observed for both (a) Ti-diffused specimen and (b) control specimen which were from same silicon wafer. Voltage swing from -6 V to -1 V. Pulse width kept at 100 μsec and the rate window was $t_1/t_2 = 1.0/9.0$ msec.

The temperature dependent cross section for the Ti related hole trap $H2$ in this specimen was found to agree with that for this same trap in Si doped with Ti during ingot Czochralski growth (Fig. 9).

The physical nature of the $H1$ and $H3$ hole traps is not known. The presumption is that they are quench-induced defect levels and not related to ampule impurities or the argon gas in the ampule. These data are in agreement with those of published quench-in defects[12–14]. However it was interesting to observe that the presence of 1 μm thick SiO_2 coating, grown in wet oxygen for 1 hr at 1200°C, over the surface of both the control specimen and the Ti-evaporated specimen prior to any heat treatment, inhibits the formation of the $H1$ and $H3$ level and the result is similar to those by Czochralski grown ingot material. This may suggest therefore that these defect levels are not related to oxygen in the original silicon or oxygen introduced during oxidation or diffusion.

5. MINORITY CARRIER LIFETIME MEASUREMENTS

Some very preliminary measurements of the minority carrier lifetimes τ_n and τ_p in p and n type Ti doped Si, respectively, have been made. The reverse recovery current technique was used for n^+p and p^+n junctions.

The temperature dependence of lifetime obtained for an n^+p diode made from Czochralski grown boron doped 3.35×10^{15} cm^{-3} and Ti doped 1.35×10^{13} cm^{-3} material is shown in Fig. 13. The excess electron lifetime is seen to be about 50 nsec at 300°K and to increase to 300 nsec at 400°K. The control specimens were of about 7 μsec lifetime. In this work no study was made of the

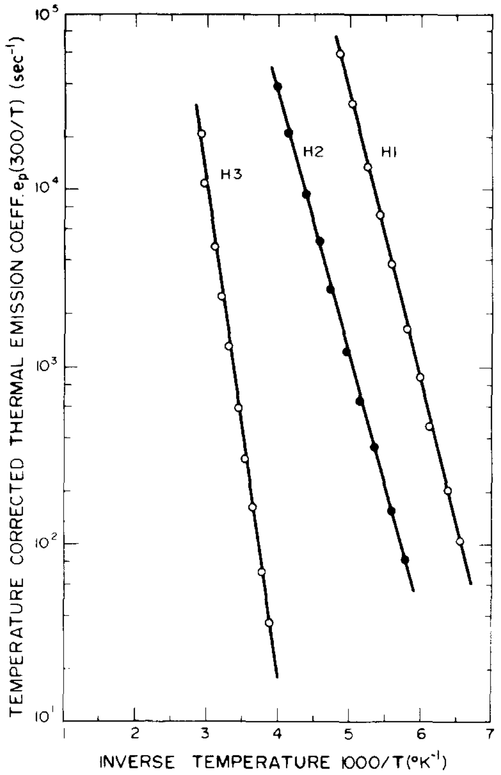

Fig. 11. Trap levels observed in Fig. 10 of titanium diffused specimen. The energy levels were determined from their hole thermal emission rates. Without correction of temperature dependence of capture cross section: $H3 = E_V + 0.55$ eV, $H2 = E_V + 0.30$ eV and $H1 = E_V + 0.33$ eV from slopes.

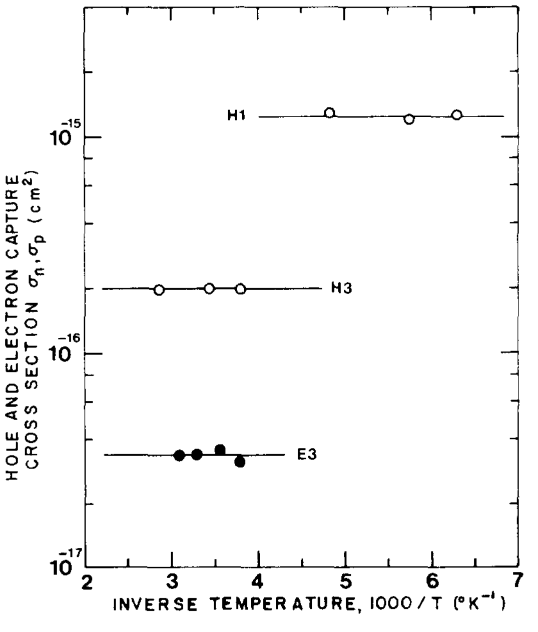

Fig. 12. Variation of capture cross section σ_p(○) for $H1$ and $H3$, σ_n(●) for $E3$ with temperature.

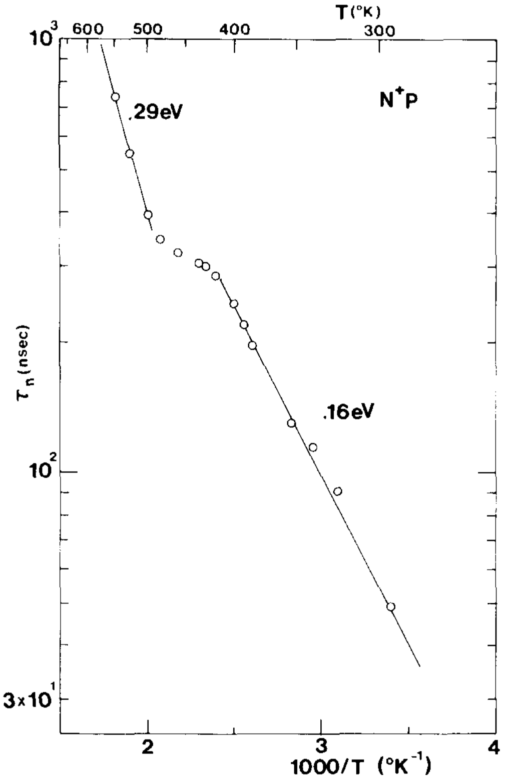

Fig. 13. The temperature dependence of lifetime obtained for an n^+p diode made from Czochralski grown boron doped $3.35\times10^{15}\,cm^{-3}$ and Ti doped $1.35\times10^{13}\,cm^{-3}$ (electrically active) material.

dependence of lifetime on Ti concentration or on injection level—the injected current density before reverse biasing was about 1.3 A per cm^2 for the results shown. The temperature dependence gives an activation energy 0.29 eV at high temperatures. In general the activation energy of lifetime depends on the Fermi level and the recombination level position in a complicated way[15], however under certain doping and temperature conditions[16] the minority carrier lifetime for a semiconductor with a recombination center at E_T may be expected to vary roughly as

$$\tau \propto \exp(-E_T/kT).$$

Hence the observed activation energy of 0.29 eV presumably involves the Ti $E_V + 0.29$ (or 0.26) eV donor level. The range of temperature over which this activation energy applies is comparable with that observed for the electron lifetime in pSi(Pt) where an $E_V + 0.32$ eV Pt donor level is involved[16].

However for the pSi(Ti) between 400 and 300°K the electron lifetime shows an activation energy of 0.16 eV. The cause is not known—although it might possibly be due to a titanium related level near a band edge. In Fig. 10 the Ti diffused specimen DLTS signature shows a small emission hump in the region of 90°K and this appears to represent a level at about $E_V + 0.16$ eV. In Czochralski grown Si(Ti) the emission hump was even more apparent. The n^+p diode for the lifetime measurements of Fig. 13 was fabricated from Czochralski doped p-Si rather than Ti diffused Si, since in diffused material somewhat less of a lifetime reduction was observed.

The results of hole lifetime measurements on a p^+n Si(Ti) diode are shown in Fig. 14. The material was Czochralski doped with a phosphorus concentration about $3\times10^{15}\,cm^{-3}$ and initial total titanium concentration about $3.5\times10^{14}\,cm^{-3}$. The active titanium concentration may have been reduced by the processing of the diode. The hole lifetime in the p^+n specimen is seen to be appreciably greater than the electron lifetime in the n^+p specimen of Fig. 13.

The activation energy of 0.26 eV at high temperatures is presumably related to the $E_C - 0.26$ (0.22) eV Ti donor level. At temperatures between 450 and 300°K the lifetime tails off and approximates a line which is of slope 0.06 eV.

These tentative results are presented to stimulate in the future the more systematic and intensive investigations needed to fully understand the effects of Ti on the minority carrier lifetimes in p and n-Si.

6. CONCLUSIONS

Titanium in silicon causes donor levels at $E_C - 0.26$ (0.22) eV and at $E_V + 0.29$ (0.26) eV and from concentration measurements these are probably associated with the same defect state. If there is an acceptor level in the bandgap it is closer to the conduction band edge than

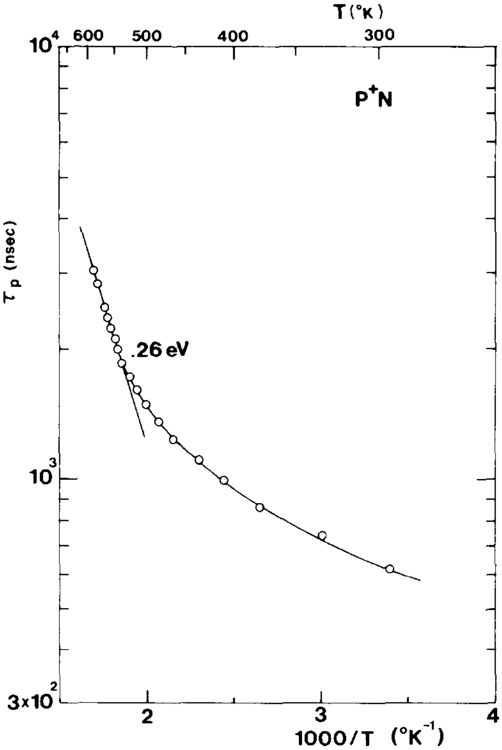

Fig. 14. The temperature dependence of lifetime obtained for a p^+n diode made from Czochralski grown phosphorus doped $3\times10^{15}\,cm^{-3}$ and Ti doped $3.5\times10^{14}\,cm^{-3}$ (total) material.

$E_C - 0.1$ eV. A 1200°C diffusion and quench produces an active center solubility of about $2\times10^{14}\,\mathrm{cm}^{-3}$. The electron capture cross section of the $E_C - 0.26$ eV level is about $3\times10^{-15}\,\mathrm{cm}^2$ at 300°K. The hole capture cross section of the $E_V + 0.29$ eV level is $1.5\times10^{-17}\,\mathrm{cm}^2$ at 300°K.

Titanium in silicon causes a considerable reduction in lifetime but extensive study is needed to understand the behavior.

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