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NEGATIVE-U FOR POINT DEFECTS IN SILICON, (U)
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1. REPORT NUMBER (6)		2. GOVERNMENT AGENCY AD-A104482		3. RECIPIENT'S CATALOG NUMBER (2)	
4. TITLE (and Subtitle) Negative-U for Point Defects in Silicon			5. TYPE OF REPORT & PERIOD COVERED Preprint		
7. AUTHOR(s) G. D. Watkins, A. P. Chatterjee, and R. D. Harris			8. CONTRACT OR GRANT NUMBER(s) (1-171)		
9. PERFORMING ORGANIZATION NAME AND ADDRESS Lehigh University Bethlehem, PA 18015			10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS		
11. CONTROLLING OFFICE NAME AND ADDRESS (15) N. 414-11-C-104			12. REPORT DATE Sep 1980		13. NUMBER OF PAGES 6
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)			15. SECURITY CLASS. (of this report) Unclassified		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited					
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)					
18. SUPPLEMENTARY NOTES This is the text of a talk given at the International Conference on Defects and Radiation Damage in Semiconductors, Oiso, Japan, September 1980.					
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Defects, silicon, rediation damage, negative-U, vacancy, interstitial boron.					
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) New evidence is presented that the lattice vacancy and interstitial boron in silicon are negative-U systems: 1) the equilibrium charge state for the vacancy in low resistivity p-type material is confirmed to be v^{++} . 2) The metastable donor level for interstitial boron at $E_c - 0.12$ eV is detected in a novel photo-DLTS experiment confirming its negative-U properties.					

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*Int. Conference of Defects and Radiation Damage
in Semiconductors, Osaka, Japan, Sept 1980
(last of papers, in press)*

NEGATIVE-U FOR POINT DEFECTS IN SILICON*

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New evidence is presented that the lattice vacancy and interstitial boron in silicon are negative-U systems: 1) the equilibrium charge state for the vacancy in low resistivity p-type material is confirmed to be V^{++} . 2) The metastable donor level for interstitial boron at $E_c - 0.12$ eV is detected in a novel photo-DLTS experiment confirming its negative-U properties.

The concept of negative-U properties in solids was first proposed by Anderson (1975) to explain the mysterious absence of paramagnetism in chemically doped chalcogenide glasses. The concept was subsequently extended to defects in these materials by Street and Mott (1975). The idea was that the energy gained by electron pairing at a defect, coupled with a large lattice relaxation, or lattice configurational change (Kastner et al. 1975), might overcome the Coulombic repulsion of the two electrons, supplying a net attractive interaction between them (negative-U) at the site. It is now generally accepted that such a phenomenon is probably the correct explanation for the properties of these glasses. However, it is interesting to note that there has been as yet no direct microscopic experimental confirmation that any defects with this property actually exist in these materials.

The first concrete experimental evidence of negative-U behavior for a defect in any solid was recently presented for the isolated lattice vacancy and interstitial boron in crystalline silicon (Watkins and Troxell 1980, Troxell and Watkins 1980). The level positions proposed for these simple radiation-produced point defects are illustrated in Fig. 1. For the vacancy, Fig. 1(a), the first donor level (0/+) at $\sim E_v + 0.05$ eV lies below the second donor level (+/++) at $E_v + 0.13$ eV. This inverted order for the levels is consistent with the suggestion by Baraff, Kane, and Schlüter (1979) who first pointed out from theoretical grounds that the greater Jahn-Teller relaxation for V^0 than for V^+ could supply the driving force for negative-U behavior. For interstitial boron, Fig. 1(b), the acceptor level (-/0) at $E_c - 0.45$ eV was proposed to lie, inverted, below the donor state (0/+), estimated at $\sim E_c - 0.15$ eV. The value $E_c - 0.12$ eV indicated in Fig. 1(b) derives from more recent results to be described in this paper. This inverted order for the levels, reflecting the stronger binding for the second trapped charge, is a characteristic of a negative-U system. It implies that the intermediate para-

*Research supported by the U.S. Navy ONR Electronics and Solid State Sciences Program, Contract No. N00014-76-C-1097.

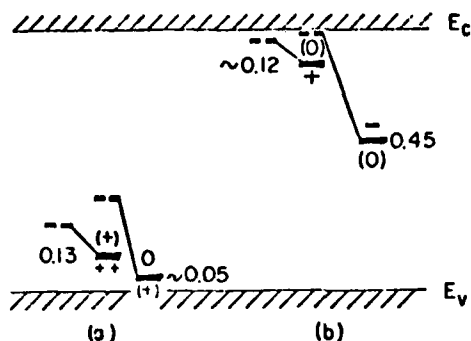
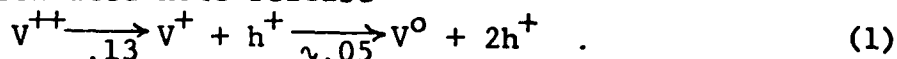


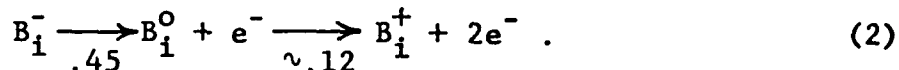
Fig 1. Level positions suggested for (a) the vacancy and (b) interstitial boron. The dashed lines indicate schematically the level positions before lattice relaxation.

magnetic charge state (V^+ or B^0) is metastable, and does not exist in thermal equilibrium.

The principal evidence presented in that work (Watkins and Troxell 1980) was based on the recognition that a negative-U defect would display unique properties in DLTS studies: For the vacancy in p-type material, DLTS monitors the thermally activated hole release



For interstitial boron in n-type material, the electron release is monitored



Here we have indicated the thermal activation barrier associated with the level position (in eV) for each emission process. In each case, the limiting process is the first charge carrier release (the deeper level); the second more weakly bound carrier emission should follow immediately. The result therefore is that only the deeper level is detected by DLTS, but because two carriers are released, the amplitude of the DLTS peak should be twice its normal amplitude. The evidence cited for this property is summarized in Fig. 2. Fig. 2(a) shows the DLTS spectrum of p-type floating zone silicon containing 10^{18} Sn/cm³, which has been irradiated at 4.2 K by 1.5 MeV electrons. The spectrum is shown, both before and after annealing at 200 K. From previous EPR studies (Watkins 1975a) and the kinetics of the annealing observed in DLTS studies (Watkins and Troxell 1980), we anticipate $\approx 100\%$ conversion of vacancies (V) to vacancy-tin pairs (V·Sn) as the vacancies diffuse through the lattice and are trapped by tin, the dominant impurity. Instead, we observe that the amplitude of the vacancy level peak at $E_v + 0.13$ eV is \approx twice the intensity of the resulting vacancy-tin peaks at $E_v + 0.07$ eV and $E_v + 0.32$ eV. Assuming that the V·Sn pair is a normal defect with one hole emission for each of its two levels (from EPR studies it is confirmed that the neutral state has no Jahn-Teller distortion (Watkins 1975c)), this was taken

as evidence that the vacancy emits two holes, and is a negative-U system.

In Fig. 2(b), we show the DLTS spectrum in n-type silicon partially counterdoped with boron, which has been irradiated at 4.2 K by 1.5 MeV electrons and subsequently annealed to 100 K. From previous EPR studies (Watkins 1976), we anticipate the principal damage products to be equal concentrations of interstitial boron, the dominant trap for mobile interstitial atoms at 4.2 K and vacancies which have been trapped either at oxygen to form vacancy-oxygen pairs (V·O) or phosphorus to form vacancy-phosphorus pairs (V·P). All three can be monitored in the figure, the presence of the V·P pairs being revealed after annealing of the interstitial boron. We note that the intensity of the interstitial boron peak at $E_c - 0.45$ eV is very close to twice the sum of those for the two vacancy-associated levels. Again this was taken as evidence that B_i emits two electrons and is also a negative-U system.

The estimates for the level positions of the shallower levels came from EPR studies of the decay of the photogenerated metastable V^+ (Watkins 1975a) and B_i^0 (Watkins 1975b) states.

In the remainder of this paper, we present results of recent new experiments on these systems to further test these ideas.

1. Vacancy

Fig. 1 implies that the stable charge state in low resistivity p-type material is V^{++} . If this is correct, photo-generation of the EPR active V^+ state with less than band gap light at temperatures below carrier freeze-out should release holes

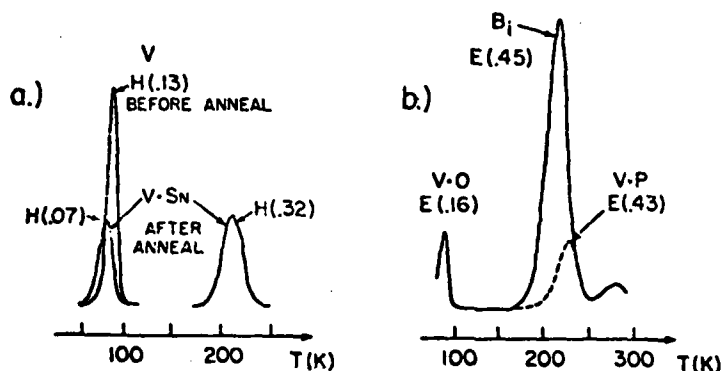


Fig 2(a) Conversion of vacancies to tin-vacancy pairs monitored by DLTS in electron irradiated p-type silicon containing $10^{18}\text{Sn}/\text{cm}^3$.

(b) DLTS of partially counterdoped n-type silicon ($1 \times 10^{16}\text{B}$, $3 \times 10^{16}\text{P}/\text{cm}^3$) after 4.2 K electron irradiation and 100 K anneal.



which will be trapped at the compensated shallow acceptors



To test this we have studied electron irradiated high quality WASO-S boron-doped material grown by Wacker Chemical Company where the internal strains are low enough to allow EPR observation of B_s^0 (Neubrand 1978) as well as V^+ . Upon photogeneration of V^+ at 4.2 K with $h\nu < 0.35$ eV, we observe a corresponding increase in the B_s^0 resonance confirming this critical aspect of the model.

An additional confirmation that the equilibrium charge state of the vacancy is not the neutral state in low resistivity p-type material comes from stress alignment studies. In heavily irradiated p-type material (high resistivity, strongly compensated) cooling in the dark from ~ 100 K under uniaxial stress was found to freeze in the vacancy alignment as monitored by EPR observation of the subsequently photogenerated V^- state (Watkins 1975a). This was successfully interpreted as reflecting the alignment properties of V^0 . We have recently repeated this experiment for lightly irradiated material (only partially compensated, Fermi level still close to the shallow acceptor level) and we find no alignment. Again this is consistent with V^{++} as the equilibrium charge state at ~ 100 K in this low resistivity material, since no Jahn-Teller distortion occurs for V^{++} .

2. Interstitial boron

The single donor state, estimated from EPR studies to be at $\sim E_c - 0.1$ eV, is deep enough so that if interstitial boron could be prepared repetitively in the metastable B_i^0 state, it could be detected directly by DLTS. Unfortunately, this won't work in the normal DLTS experiment because at the low temperature required to see the shallow level, repetitive trap filling pulses, no matter how short, will eventually convert all of the interstitial boron to B_i^- , removing them from the experiment.

We have avoided this difficulty by illuminating the n-type diodes with penetrating light (through a room temperature silicon filter) to photoionize the B_i^-



preventing accumulation of B_i^- during the DLTS experiment. (The light level is adjusted to give a decay time ~ 25 ms which is $\sim 1/3$ the period between trap filling pulses. This assures that no B_i^- is present at the beginning of each pulse.) The result is shown in Fig. 3(a). In the presence

of the light, a new peak is observed. Our preliminary studies of the temperature dependence of its emission rate locates its level position at $E_C - 0.12$ eV, as indicated in Fig. 1. This peak disappears upon thermal annealing at ~ 230 K, or injection annealing at ~ 150 K in $\sim 1:1$ correspondence with the disappearance of the $E_C - 0.45$ eV interstitial boron peak. In addition, as seen in Fig. 3, the amplitude of the peak decreases with increasing pulsewidth, an anomalous result for a normal level. On the other hand, this is a unique and necessary signature of a negative-U defect, the longer pulse producing in this case more of the deeper two-electron B_i^- state and less of the shallow one-electron B_i^0 state.

The concentration of B_i^- present after each pulse can also be measured in the DLTS experiment by monitoring the amplitude of the photoinduced decay of the $E_C - 0.45$ eV level. (The boxcar is tuned to the 25 m sec photo-decay rate.) In Fig. 4 we show the concentration of B_i^- estimated in this way along with the concentration of B_i^0 estimated from the height of the $E_C - 0.12$ eV peak, vs. pulse width. The complementary behavior and the constancy of the sum demonstrates dramatically the fact that they are inverted negative-U levels associated with the same defect.

3. Summary

In summary, we have presented what we believe to be unambiguous proof that interstitial boron is a negative-U system. We have detected the metastable donor state level directly and locate its position at $\sim E_C - 0.12$ eV. In addition, we have confirmed that V^{++} is the stable charge state in low resistivity p-type material, one of the predictions

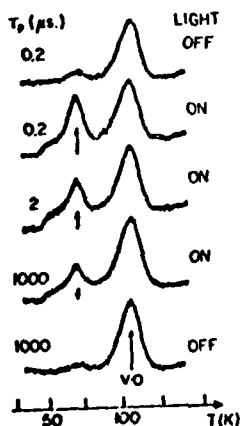


Fig 3. The metastable B_i^0 donor level at $\sim E_C - 0.12$ eV observed in the presence of light.

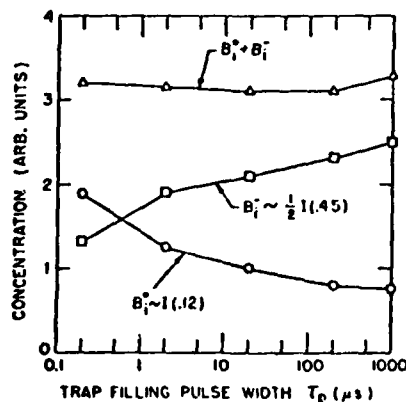


Fig 4. The concentrations of B_i^0 and B_i^- vs. trap filling pulse width τ_p , estimated from the intensities I_p of the $E_C - 0.12$ and $E_C - 0.45$ eV peaks in the presence of light.

of Baraff et al. (1979) and an essential feature of the negative-U model for it. Direct electrical detection of its single donor state remains for the future.

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