THE CHEMISTRY AND NEUTRALIZATION OF BORON BY HYDROGEN PASSIVATION IN SILICON

Lawrence L. Kazmerski, Art J. Nelson and Ramesh G. Dhere*

Solar Energy Research Institute
1617 Cole Boulevard
Golden, Colorado 80401 EUA
*On leave from Instituto Militar de Engenharia, Brasil

The interaction between the shallow acceptor boron and hydrogen in single crystal, polycrystalline and amorphous Si is investigated. Low-temperature SIMS depth -compositional profiles indicate a distinct interaction between the boron concentration and the hydrogen penetration in single crystals and at grain boundaries. The bonding of the H is identified to be directly to the Si rather than to the B. This is confirmed by infrared measurements. Hydroxyl-group donding as part of the electrical neutralization of the B is also reported at oxygen-rich Si grain boundaries. No similar relationship between P concentration and H penetration is observed. In amorphous material, the effect of the B-doping level has only a limited effect on the hydrogen penetration which seems to be controlled instead by structural diffusion mechanisms.

Silício, Espectroscopias de análise de superfície, Contornos de grão

1. INTRODUCTION

Amorphous, poly- and single-crystalline silicon have numerous electronic applications, ranging from submicron-size high-speed integrated components to multi-centimeter dimensioned solar cells. As research continues on this—the *most* investigated of the semiconductors—the introduction of new device structures continues, and the performance of the devices themselves improves. Examples of these advances in the photovoltaic area include a variety of single-crystal Si cells with greater than 20% conversion efficiency [1-3], highlighted by the recently reported single-crystal cell with a verified efficiency of *21.9%* (AM1.5 spectrum, 25ºC, 100 mW/cm^2 irradiance). A significant contributing factor has been the *increased understanding and control* of impurities in the semiconductor

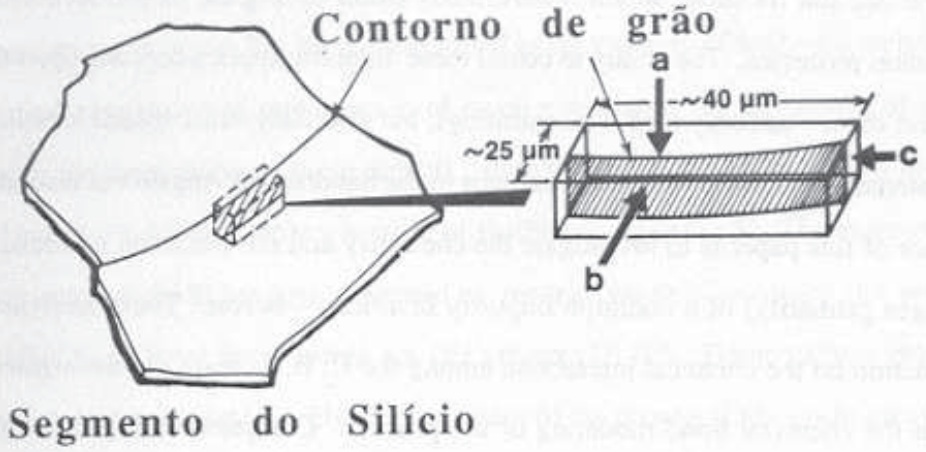

Fig. 1. Representação de SIMS volumetrico.

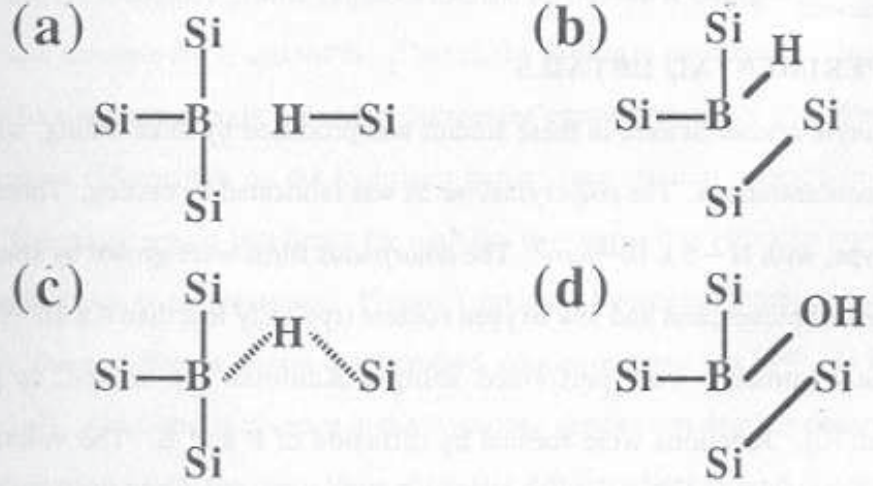

Fig. 2. Modelos de boro neutralisado em Si. (a) Si-H; (b) B-H; (c) "ponte"; (d) hidroxyl.

material itself [4-8]. This is both for purposely-placed impurities for doping and electrical passivation, and for those which inadvertantly occur during the Si-production or device fabrication processes. The ability to contol these impurity species depends upon the ability to detect them—not only their concentrations, but also their exact spatial locations within the material or at critical interfaces, perhaps to the hundreds of Angstroms resolution. The *purpose* of this paper is to investigate the chemistry and the electrical neutralization (by hydrogen primarily) of a common impurity in silicon—***boron***. These analyses provide information on the chemical interaction among the H, B, Si and O in the semiconductor, and on the chemical bond-modeling of the process. Comparative depth-compositional profiling using Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS) is employed. In addition, specially-developed *volume-indexed surface analysis* techniques [9], which provide the presentation of compositional data along any selected plane or line, or at any point within a specific, pre-selected microvolume, are utilized to provide the direct and accurate determinations of the chemistry variations within the material/device.

2. EXPERIMENTAL DETAILS

The *single-crystal* Si used in these studies was produced by float-zoning, with specific B and P concentrations. The *polycrystalline* Si was fabricated by casting. These substrates were p-type, with $N \sim 5 \times 10^{16}/cm^3$. The *amorphous* films were grown by standard glow discharge techniques, and had low oxygen content (typically less than $6 \times 10^{18}/cm^3$). The hydrogen treatments were performed using a Kaufman ion source, as previously described[10]. Junctions were formed by diffusion of P and B. The volume-indexed SIMS and AES were performed in a CAMECA IMS-3f Ion Microprobe and Perkin-Elmer Model 595 and 600 Multiprobes. The instrumentation and techniques, described previously [9-12] and illustrated in Fig. 1 for a grain boundary analysis, provide the digital acquisition of SIMS and/or AES data throughout a selected microvolume, coding this information for ion or element type, spatial location, and concentration (signal level). The software permits the operator to selectively display the information for any point, along any line, or on any plane within the analysis microvolume after a *single* analytical operation.

3. RESULTS AND DISCUSSION

The incorporation of hydrogen at crystalline defects (e.g., grain boundaries) has been previously reported [11-15], and *differences* between the hydrogen bonding in heat-treated and non heat-treated samples has been documented using a variety of analytical techniques. The electrical passivation of impurities is of equal importance for the control of device properties to the passivation of those defects. In this respect, atomic hydrogen has also been used to *electrically neutralize* a number of shallow acceptors in Si. The incorporation of the hydrogen into the Si has been explained by **several models** involving the bonding of H to either Si or B, or the bonding via OH groups [16-20]. These various proposed bonding schemes are indicated in Fig. 2. The intent of the present studies is to investigate the passivation of electrically active B in crystalline Si, and to accurately identify the bonding mechanisms involved in this process.

Spreading resistance profiles have been used by Pankove *et al.* [16,21] to show that there is an *interaction* between the boron content (i.e., the concentration level) of the Si and the hydrogen penetration. Treatment in atomic hydrogen increases the resistivity of the B-doped Si, and the resistance profile suggests that the higher the B-background, the greater the interaction between the H and the B. (That is, the hydrogen penetration is by diffusive transport which is *increasingly slowed* by *increasing* concentrations of B.) However, no direct chemical information on the hydrogen-boron concentration interaction has been reported. The major reason that limits the inability to observe this effect by conventional analysis techniques is ***temperature***. Figure 3 presents hydrogen depth-profiles (using SIMS) for three different boron background concentrations ($6x10^{16}$, $1x10^{18}$, and $9.8x10^{18}/cm^3$). Almost no difference in the hydrogen penetration depth is observed using room-termperature SIMS for these three distinctly different background concentrations. However, when the same samples are cooled to 80K during analysis, the anticipated differences are noted. Figure 4 shows these profiles. Thus, the low-temperature depth profiles show that the diffusion of atomic H into the Si decreases with increasing B-concentrations, giving evidence for the predicted B-H interactions. The same experiments were performed on P-doped samples, in order to ensure that the effect was not either a

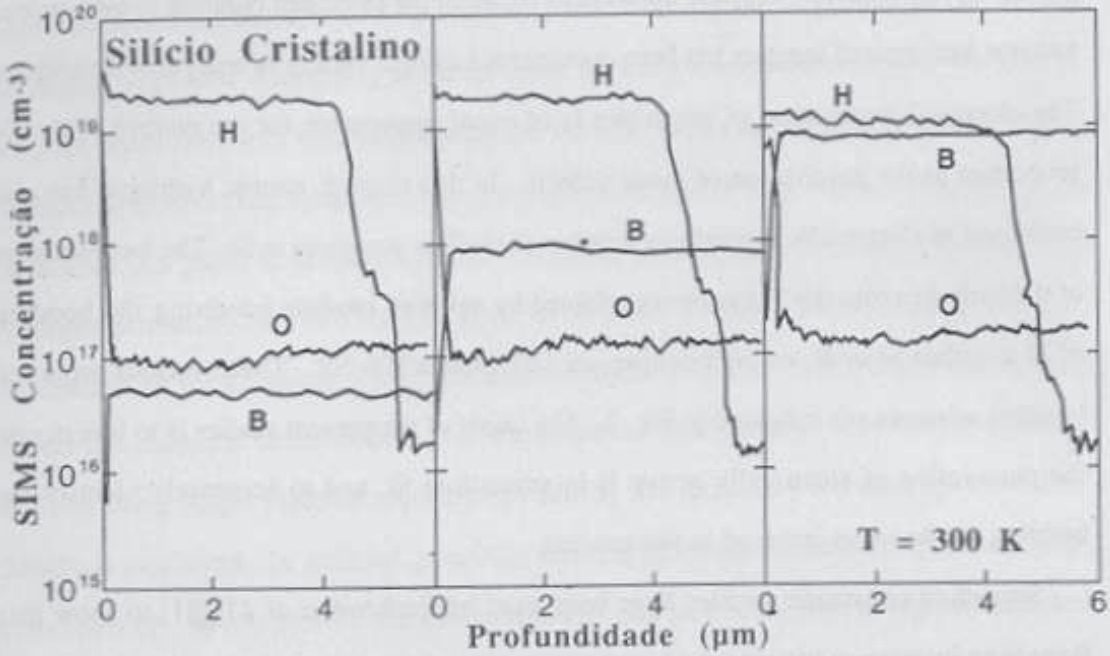

Fig. 3. Perfis SIMS de hidrogenio para concentrações de boro em silício monocristalino. (a) $6x10^{16}$; (b) $1x10^{18}$; (c) $9.8x10^{19}/cm^3$. T = 300 K.

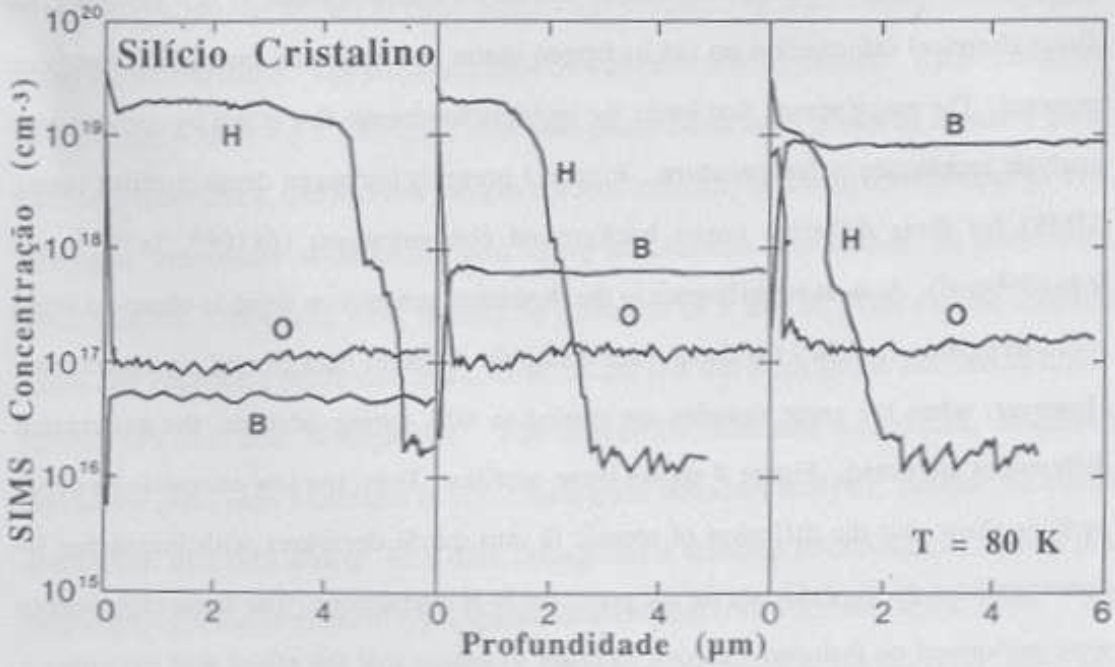

Fig. 4. Perfis SIMS de hidrogenio (mesma na Fig. 3, mais T = 80 K)

general concentration effect or a general temperature effect. Figure 5 presents the results, with the measurement performed at 80K. The hydrogen profile is *unaffected* by the P-background, shown for 10^{17}, $8x10^{18}$, and $6x10^{19}/cm^3$. The *method of incorporating* the B is not important. Figure 6 shows the low-temperature profiles for B-diffused layers, and the same hydrogen dependence on the B-background concentration is evident. However, the *crystallinity* does seem to be a factor. For H diffusion into a B-doped amorphous Si film (Fig. 7), only a very slight effect is noticed—even at the low temperature. The higher inherent diffusivity of the B for the amorphous medium (compared to crystalline diffusion) seems to dominate the process.

How the hydrogen interacts with the silicon and the boron is very important. The four major models of Fig. 2 have been proposed to explain the neutralization. In the first, proposed by Sah *et al.* [18], the H is bonded directly to the B. This requires the reconstruction of dangling bonds between adjacent Si atoms. A stretching mode at about 2560 cm^{-1} would be expected in the infrared spectrum. Another model has a hydrogen "bridging" between the Si and the B atoms [19]. An IR feature at 1985 cm^{-1} would be expected from this scheme. Pankove *et al.* [17,21] have proposed that the H is tied not to the B, but to one of the four Si atoms surrounding the substitutional boron atom—satisying all the valence bonds. The Si-H vibration in the IR spectrum would occur between 1850 and 2000 cm^{-1}. The final model includes a possible role of oxygen through hydroxyl-group bonding, which is known to exist in both single and polycrysalline Si. The nature of the bonding is investigated in this paper by complementary IR data on the same samples examined by the surface analysis. In Fig. 8a, a low oxygen content sample, the data show a peak at about 1880 cm^{-1}. This is the commonly reported Si-H, or mono-hydride, response. This agrees with the model proposed by Pankove et al., or Fig. 2c. The anticipated features for the B-H and bridge-bonding schemes are <u>not</u> observed. In Si having a *greater* oxygen concentration (by about 1 order of magnitude), a peak at 1800 eV is also present in the IR spectrum (Fig. 8b), and is ascribed to ***hydroxyl bonding***. These data are similar to those observed at oxygen-rich grain boundaries in polycrystalline Si material.

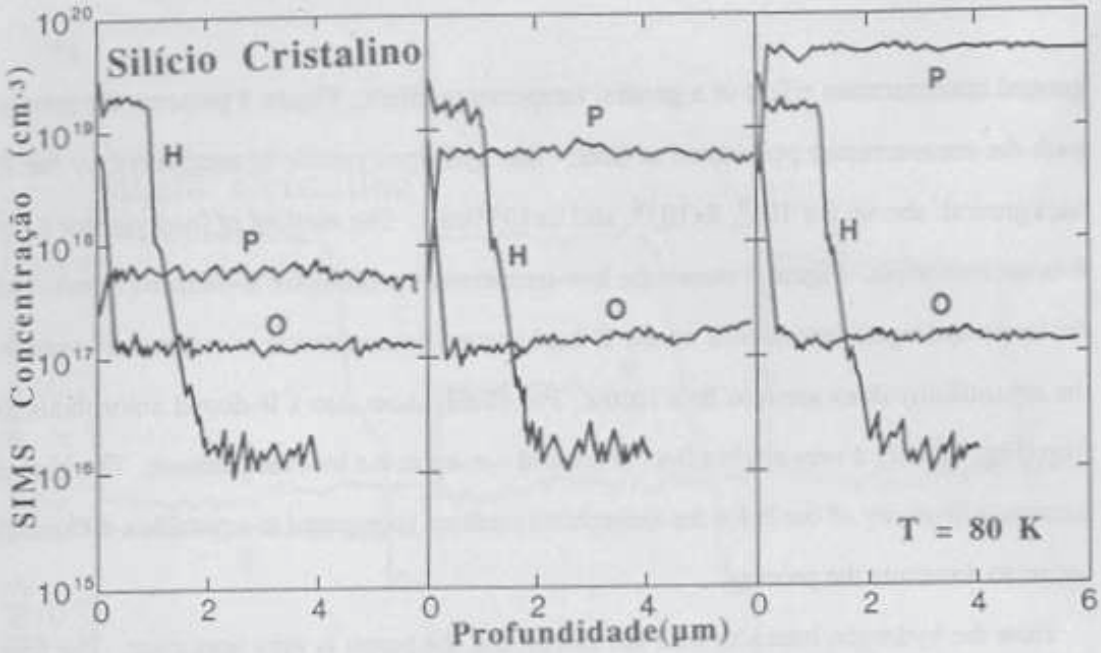

Fig. 5. Perfis SIMS de hidrogenio para concentrações de P: (a) $1x10^{17}$; (b) $8x10^{18}$; (c) $6x10^{19}$ /cm^3. T = 80 K.

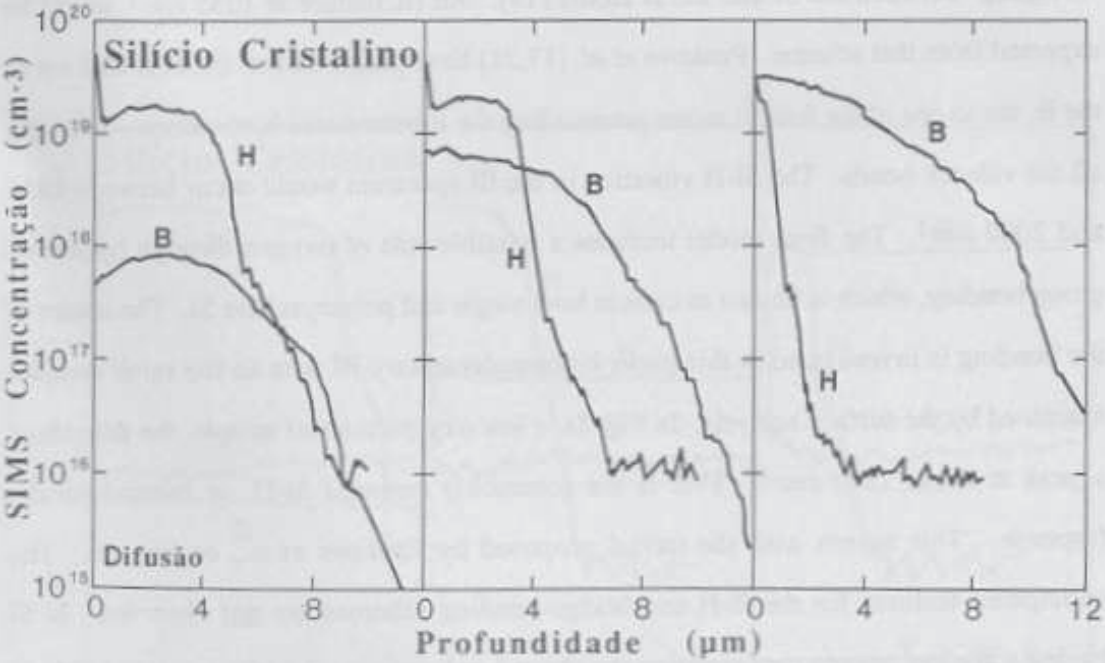

Fig. 6. Perfis SIMS de hidrogenio para camadas difundidas com boro.

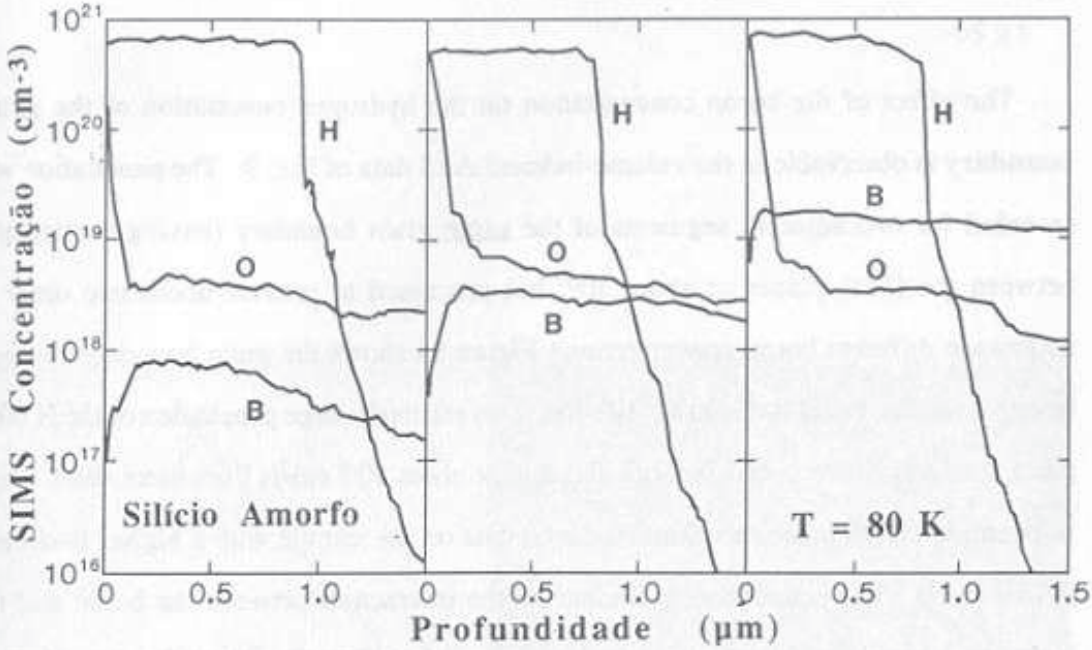

Fig. 7. Perfis SIMS de hidrogenio para concentrações de boro em silício amorfo.

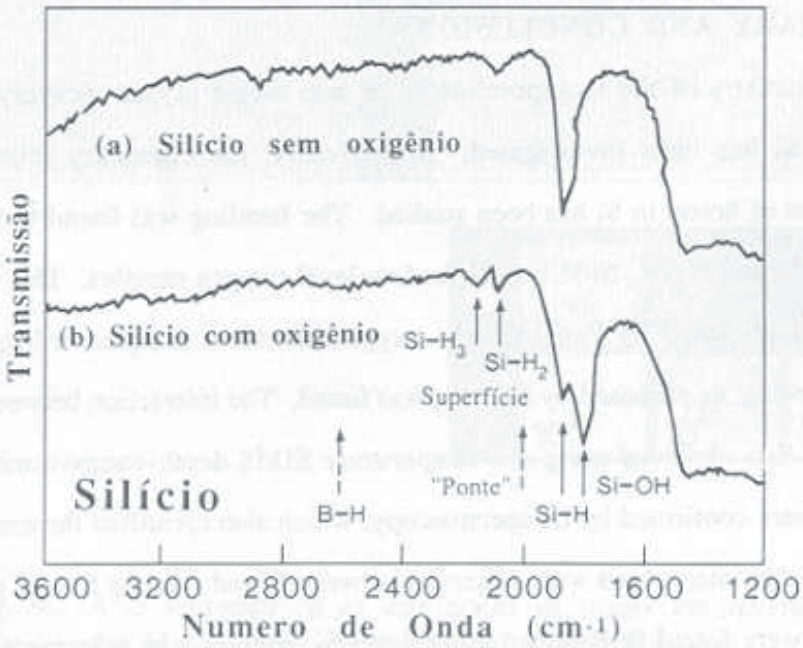

Fig. 8. Espectro infra-vermelho para (a) deficiente em oxigenio; e (b) excesso em oxigenio.

The effect of the boron concentration on the hydrogen penetration of the **grain boundary** is observable in the volume-indexed AES data of Fig. 9. The penetration was recorded for two adjacent segments of the same grain boundary (having a mismatch between the (111) planes or about 30°) but processed to provide about one order of magnitude different boron concentration. Figure 9a shows the grain boundary segment having a *smaller* initial B-content (~10^{17}/cm^3). A relatively large penetration of the H takes place, with a diffusion coefficient calculated to be about 10^{-6} cm^2/s from these 400°C data. In contrast, Fig.9b presents volume-indexed data on the sample with a *higher* B-content (~10^{18}/cm^3). The penetration is *limited* by the interaction between the boron and the hydrogen—as predicted by the Pankove bonding model. The effective diffusion coefficient is some two orders of magnitude less at the 400°C temperature. Thus, the presence of this acceptor at the defect can control the chemical properties of the region. It is important, therefore, to know the exact impurity content of not only the crystal, but also the defects when evaluating the diffusion and passivation processes.

4. SUMMARY AND CONCLUSIONS

The chemistry of the incorporation of H into single crystal, polycrystalline and amorphous Si has been investigated. *Specifically,* the chemistry involved in the neutralization of boron in Si has been studied. The bonding was found to be primarily between the Si and H (i.e., Si-H bonds) for low-level oxygen samples. This corresponds to the model proposed by Pankove. In oxygen-abundent samples, a high degree of hydroxyl bonding, as proposed by Hansen, was found. The interaction between the H and the Si and B was observed using *low-temperature* SIMS depth-compositional analysis. These data were confirmed by IR spectroscopy, which also identified the exact nature of the bonding. No interactions were observed between H and P in the Si, and only limited interactions were found in B-doped amorphous Si samples. In polycrystalline Si, the interrelationship between the boron concentration and the hydrogen penetration was observed at grain boundaries using volume-indexed AES.

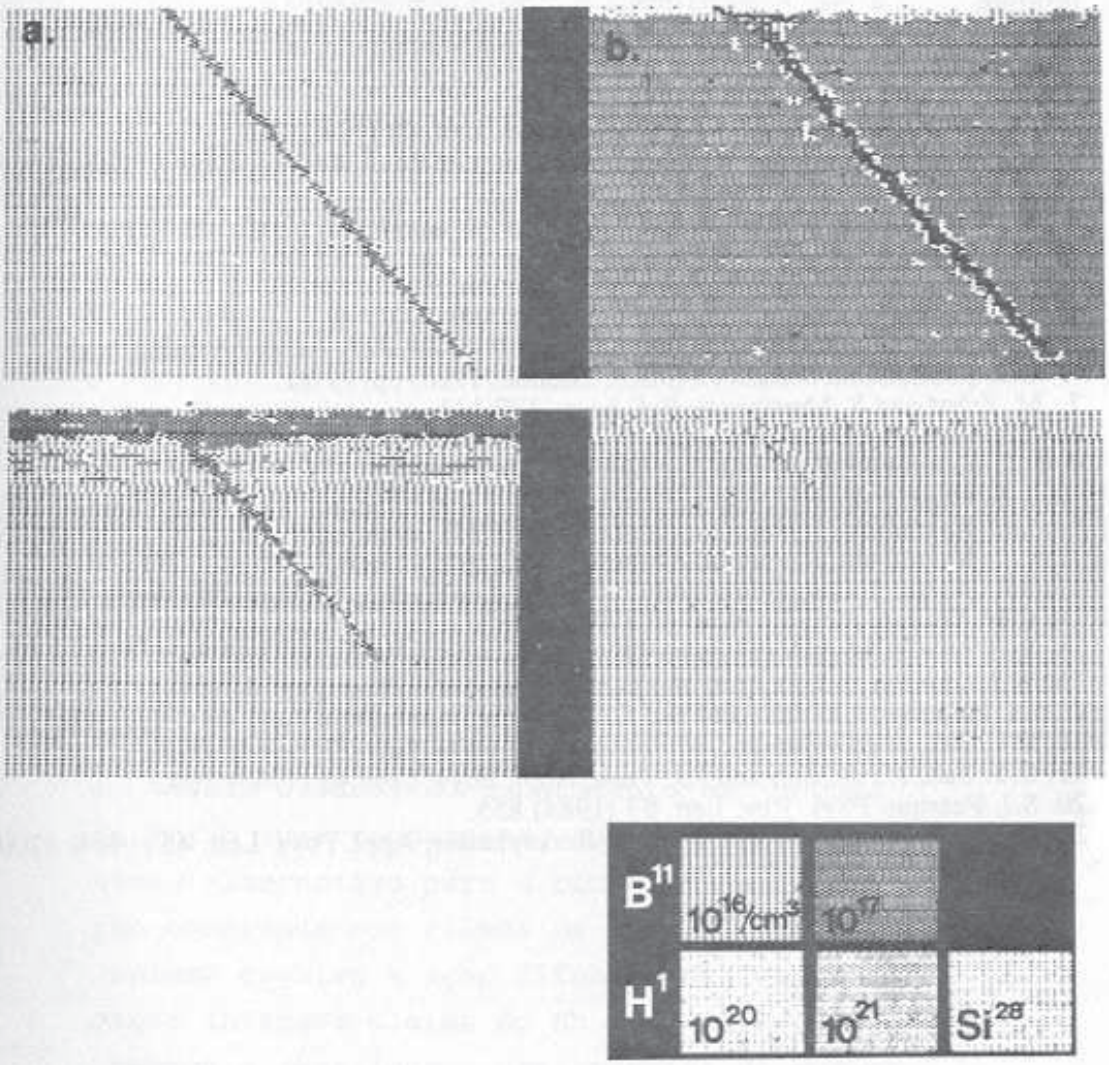

Fig. 9. AES volumetrico de contornos de grãos em silício. (a) boro (~$10^{17}/cm^3$); (b) boro (~$101^8/cm^3$).

Acknowledgements

The authors wish to express their sincere appreciation to the members of the SERI Photovoltaic Devices and Measurements Branch, especially A. Nelson, S. Asher, A. Franz, and N. Burnham. This work was supported in part by the U.S. Department of Energy under Contract No. DE-AC02-82CH10093 with the Solar Energy Research Institute.

4. REFERENCES

1. A.W. Blakers and M.A. Green, Appl. Phys. Lett. **48** (1986) 215.
2. See, for example, *Proc. 7th SERI/DOE Advanced R&D Meeting*, Denver, Solar Cells (in press).
3. See, for example, *Proc. 18th IEEE Photovoltaic Specialists Conf.*, Las Vegas (IEEE, New York; 1986).
4. S. Martinuzzi, Appl. Phys Lett. **47** (1985) 376.
5. D.S. Ginley and D.M. Haaland, Ref. 3, pp. 999-1002.
6. L. Ammor and S. Martinuzzi, *Proc. MRS Europe 84, Poly-micro-crystalline and Amorphous Semiconductors* (MRS, London; 1985) pp. 77-81.
7. M. Zehaf and S. Martinuzzi, Ref. 6, pp. 137-141.
8. C. Dube and J.I. Hanoka, Appl. Phys. Lett. **45** (1984) 1135.
9. L.L. Kazmerski, Rev. Bras. de Apl. de Vacuo **5** (1985) 271.
10. L.L. Kazmerski, Ref. 3, pp. 72-86
11. L.L. Kazmerski, J. Vac. Sci. Technol. A (1986) (in-press).
12. L.L. Kazmerski, J. Vac. Sci. Technol. A **3** (1985) 1287.
13. J.K.G. Panitz, D.J. Sharp, and C.R. Hills, J. Vac. Sci. Technol. **20** (1982) 430.
14. C.H. Seager, J. Appl. Phys. **52** (1982) 3960.
15. R.H. Micheels, A. Vayman and J. Hanoka, Appl. Phys. Lett. **46** (1985) 527.
16. W.L. Hansen, S.J. Pearton and E.E. Haller, Appl. Phys. Lett. **44** (1984) 606.
17. J.I. Pankove, P.J. Zanzuchi and C.W. Magee, Appl. Phys. Lett. **46** (1985) 421.
18. C.T. Sah, J.Y.C. Sun and J.J. Tzou, Appl. Phys. Lett. **55** (1984) 1525.
19. C.T. Sah, J.Y.C. Sun and J.J. Tzou, Appl. Phys. Lett. **43** (1983) 204.
20. S.J. Pearton, Phys. Rev. Lett. **53** (1984) 855.
21. J.I. Pankove, R.O. Wance and J.E. Berkeyheiser, Appl. Phys. Lett. **45** (1984) 1100.