Title

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DISCLAIMER

The Effects of Dopants and Defects on Light-induced Metastable States in Hydrogenated Amorphous Silicon

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Using photothermal deflection spectroscopy we measure the optical absorption of light-induced metastable defects in undoped and doped a-Si:H. We observe an enhancement in the gap-state absorption after illumination which we show is due to the creation of new silicon dangling bond defects and not to a shift in the Fermi level. The results provide evidence that the light-induced defects are related to dopants, and imply that breaking Si-Si bonds may not be the primary mechanism for creating the defects.

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An intriguing property of many amorphous semiconductors is that they exhibit metastable defect states. For both the chalcogenide glasses and hydrogenated amorphous silicon (a-Si:H), prolonged illumination creates defect states which disappear upon annealing. In the case of a-Si:H, these metastable states (Staebler-Wronski effect) alter various properities such as the conductivity,[1] and the luminescence.[2] Yet, despite extensive research,[3] they are still not well understood. Although silicon dangling bond defects have been implicated, the question remains as to whether the apparent increase in the number of these defects is due to a shift in the Fermi level,[4] or to the creation of new defects upon illumination.[5] Another significant issue is the connection between already existing (annealed state) defects and dopants, and those defects induced by illumination. In this letter we report optical absorption studies using photothermal deflection spectroscopy (PDS),[6] of the light-induced defects in a-Si:H. Since the measurement is insensitive to the position of the Fermi level, both the change in defect density due to illumination, and the evergy level of the defect can be determined. The results show that <u>new</u> silicon dangling bond defects are created by illumination,[7] and provide evidence that the metastable centers appear to be associated with dopant defects.

The a-Si:H films were undoped, singly doped and fully compensated, and were deposited by glow discharge under a wide range of deposition conditions.[8] The singly doped samples contained boron or phosphorous concentrations ranging from 10^{-6} to 10^{-2} , and the compensated sample contained 10^{-3} of both boron and phosphorous. Two undoped samples had oxygen intentionally introduced during deposition. The illumination-anneal cycle consisted of exposing the a-Si:H films to ~1.0 W/cm^2 of

unfiltered light from a quartz tungsten halogen lamp for typically 1.5 hours. Annealing was achieved by heating the films to >150 C for 1.5 hours under vacuum in the dark. The absorption spectra taken from both the front and back (substrate) sides were identical, indicating that the observed light-induced enhancement in sub-gap absorption was not due to surface changes. The absorption measurement itself had no detectable effect on either the annealed or illuminated state.

Figure 1 shows that exposure to light enhances the gap-state absorption, and annealing restores the absorption to its original dark value. The enhancement is consistently reproducible when the illumination-anneal cycle is repeated several times. Previous work has demonstrated that the magnitude of gap-state absorption in a-Si:H provides a direct measure of silicon dangling bond defect density, N_s .[9] Using the same procedure for the change in optical absorption, we quantitatively determine the change in the defect density between the annealed and illuminated states, ΔN_s . For the undoped material, ΔN_s is approximately 10^{16} cm^{-3}, which agrees with both our electron spin (ESR) measurements, and those of Dersch et al.[5] The agreement demonstrates that the optical cross section of the light-induced defect is ~1.2 x 10^{-16} cm^2. By comparing the experimental absorption spectra with calculated spectra generated from density-of-states models, the defect energy level is determined to be ~1.25eV below the conduction band. Since the energy of the defect and its cross section are identical to those measured for silicon dangling bond defects, we conclude that the change in sub-gap absorption is due to silicon dangling bond defects. Little or no change is seen in the exponential absorption (Urbach) edge.

Figure 2 shows that the light-induced defects scale with dopant concentration over a wide range of doping levels. The ratio ΔN_s / N_s is found to be independent of doping level to within a factor of 2. Thus, the effect is largest for high doping, unlike the case of conductivity changes.[10] The fully compensated sample exhibited the least enhancement, $\lesssim 10^{15}$ cm^{-3} defects, which is an order of magnitude smaller than for the undoped material. Studies of the effects of compensation will be reported elsewhere. In the case of undoped material, the increase in defect density, ΔN_s, is constant to within a factor of 2-3, independent of the initial defect density, as seen in figure 3.

The results unambiguously show that the increase in defect density is not due simply to a shift in the Fermi level towards midgap upon illumination. A shift in the Fermi level, without any change in dangling bond defect density, results in less sub-gap absorption rather than the observed increase. Further, by successively increasing the dopant concentration, the Fermi level moves into the band tails so that after illumination it is still in a region of <u>smaller</u> dangling bond density. Consequently the effect should decrease with increased doping, which is the opposite of what we observe. Since Fermi level motion alone cannot account for the observed changes, we conclude that illumination creates new dangling bond defects.

Recently, Lang <u>et al</u>.[4] have used deep level transient spectroscopy (DLTS) to study the light-induced changes in phosphorous doped a-Si:H. They conclude that after illumination there is no change in the density of states in the upper half of the gap. Instead they interpret their observations as due to motion of the Fermi level. Our results clearly

show that this is not the case.

From their DLTS data, Lang et al. deduce a large increase of about 10^{18} cm^{-3} in donor-like states at 0.5eV above the valence band. A large change in the density of states 1.6eV below the conduction band cannot produce significant changes in the absorption at 0.6eV. Instead, their density of states change would alter the slope of the Urbach edge. However, the optical absorption spectra exhibit no change in the Urbach edge, which in the case of a-Si:H is dominated by the valence-band edge.[11] This result was confirmed by a series of photoinduced absorption studies which probe the valence band tail.[12] There was no change in the decay rate between the illuminated and annealed states. Thus, we conclude that the light-induced states do not significantly alter the valence band tail.[13] In addition, recent drift mobility experiments found no evidence for light-induced hole traps, indicating that the valence band is not modified by illumination.[14]

In terms of the mechanism for creating the dangling bonds, the results imply that the light-induced defects do not result from breaking weak Si-Si bonds. One would expect ΔN_s to be relatively large for high defect density undoped material which has substantial strain disorder (as evidenced by a broad Urbach edge), and consequently a large number of weak Si-Si bonds. Yet for undoped material ΔN_s is constant, independent of disorder. Thus, for the undoped material, the light-induced defects may be associated with residual impurities such as oxygen, nitrogen, or carbon. On the other hand, the fact that for singly doped material, the ratio ΔN_s / N_s is constant, independent of thickness, dopant type and concentration, implies that the light-induced

defects are closely related to doping-induced defects or dopant-defect complexes.

Finally, there are several implications regarding solar cell fabrication. When air is let into the chamber during preparation, the cell exhibits an even larger efficiency drop after prolonged illumination, which again can be annealed away.[15] The conclusion that light-induced defects are impurity related is consistent with this observation. In addition, for p-i-n solar cells, illumination results in a fall off in the blue response.[16] Here, the doped outer layer will have the largest density of light-induced defects. Consequently photons with short penetration depths will be strongly affected.

In summary we have observed an enhancement in the gap-state absorption after illumination, which disappears upon annealing. We attribute this enhancement to the creation of new silicon dangling bond defects. For doped material the new dangling bonds are a constant fraction of the pre-existing defects. The results imply that the light-induced defects may not be related to weak Si-Si bonds as has been suggested, but rather to impurities or other defects in the films.

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References

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(1) D.L. Staebler and C.R. Wronski, Appl. Phys. Lett 31, 292 (1977); D.L. Staebler and C.R. Wronski, J. Appl. Phys. 51, 3262 (1980)

(2) J.I. Pankove and J.E. Berkeyheiser, Appl. Phys. Lett. 37, 705 (1980).

(3) for a review of the effect, see for example D.E. Carlson, Solar Energy Materials 8, 129 (1982) ; and J.I. Pankove, ibid. 141, and references therein.

(4) D.V. Lang, J.D. Cohen, J.P. Harbison, and A.M. Sergent, Appl. Phys. Lett. 40, 474 (1982).

(5) H. Dersch, J. Stuke, and J. Beichler, Appl. Phys. Lett. 38, 456 (1981).

(6) W.B. Jackson, N.M. Amer, A.C. Boccara, and D. Fournier, Appl. Optics 20, 1333 (1981).

(7) A. Skumanich, N.M. Amer, and W.B. Jackson, Bull. Am. Phys. Soc. 27, 146 (1982); N.M. Amer, A. Skumanich, and W.B. Jackson, in Proc. of 16th Intl. Conf. on the Phys. of Semiconductors, Montpellier, France 1982, edited by M. Averous, (North-Holland, Amsterdam 1983), pp. 897-898.

(8) R. Street, J.C. Knights, and D.K. Biegelsen, Phys. Rev. B 18, 1880 (1978).

(9) W.B. Jackson and N.M. Amer, Phys. Rev. B 25, 5559 (1982).

(10) M.H. Tanielian, N.B. Goodman and H. Fritzsche, J. de Phys. 42 suppl. 10, C4-375 (1981).

(11) T. Tiedje, J.M. Cebulka, D.L. Morel, and B. Abeles, Phys. Rev. Lett. 46, 1425 (1981).

(12) D.R. Wake and N.M. Amer, Phys. Rev. B 27, 2598 (1983).

(13) A. Skumanich, D.R. Wake, and N.M. Amer, Bull. Am. Phys. Soc. 28, 257 (1983).

(14) R.A. Street, Appl. Phys. Lett. 42, 507 (1983).

(15) D.E. Carlson, J. Vac. Sci. Technol., 20, 290 (1982).

(16) D.L. Staebler, R.S. Crandall, and R. Williams, Appl. Phys. Lett. 39, 733 (1981).

Figure Captions

Figure 1: The effect of illumination on gap-state absorption of undoped a-Si:H.

Figure 2: The dependence of the light-induced defect density, ΔN_s, on dopant concentration.

Figure 3: The dependence of the light-induced defect density, ΔN_s, for doped and undoped material.

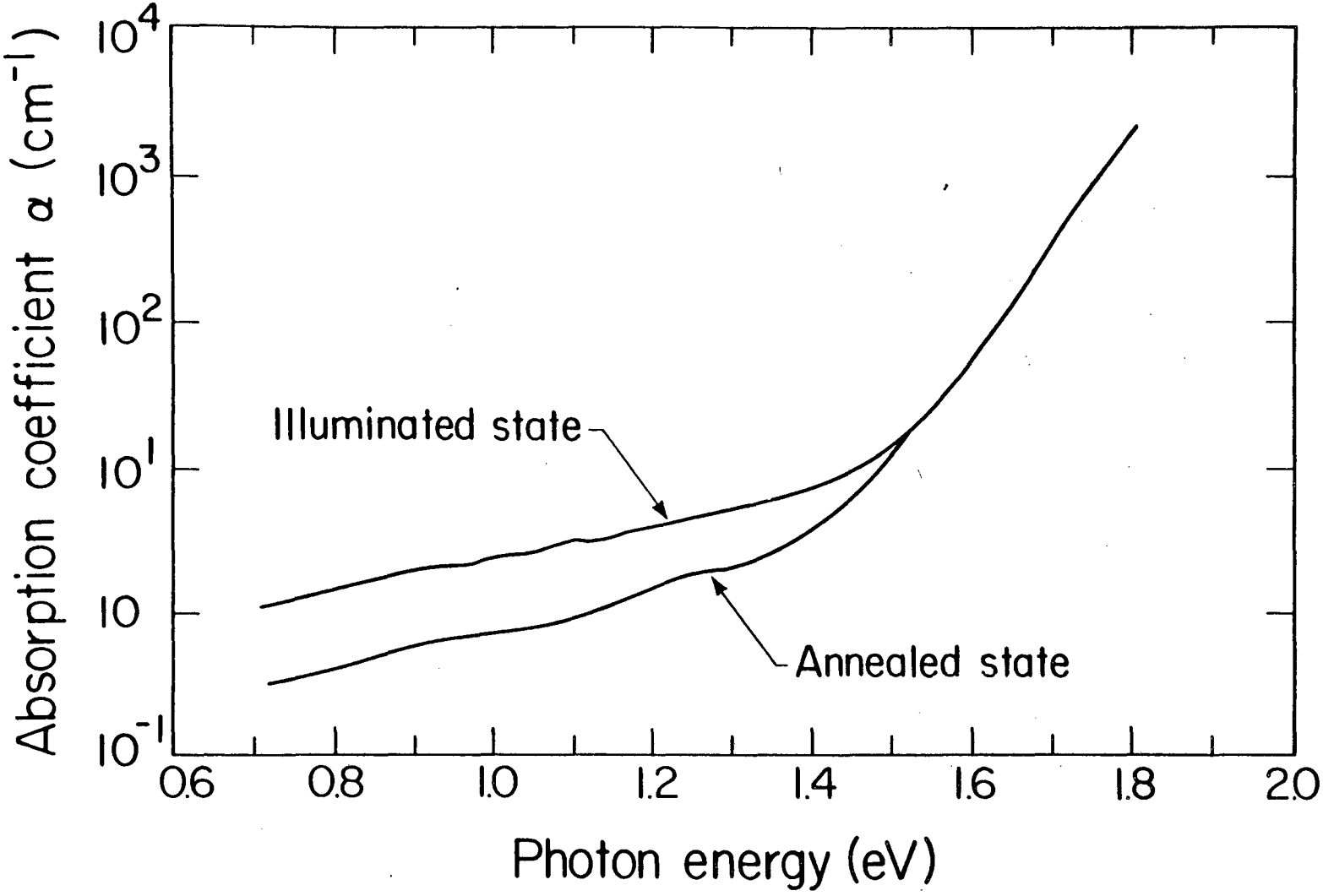

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Fig. (1)

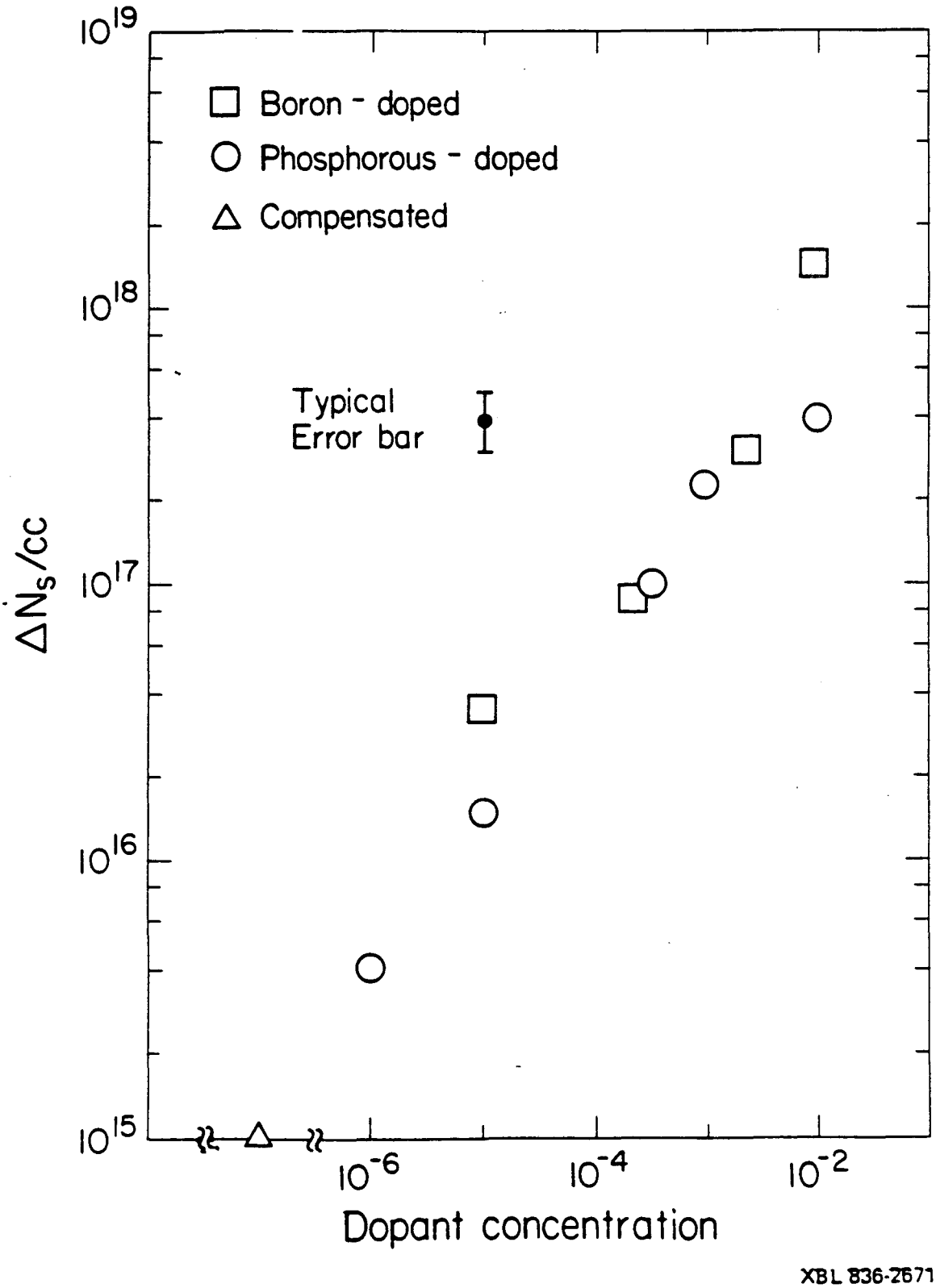
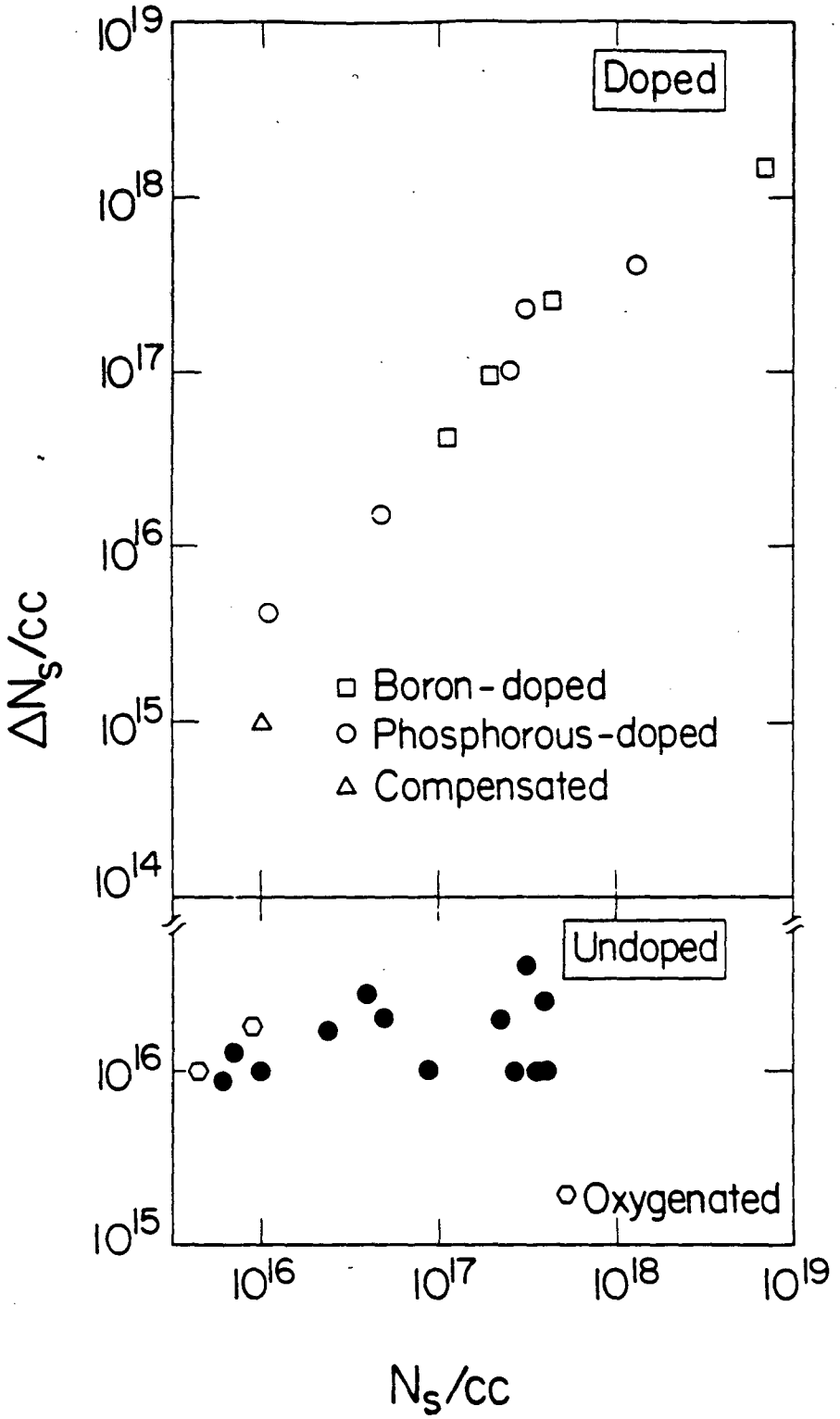

Boron - doped
Phosphorous - doped
Compensated
Typical
Error bar
10^{19}
10^{18}
10^{17}
10^{16}
10^{15}
$\Delta N_s/cc$
10^{-6}
10^{-4}
10^{-2}
Dopant concentration
XBL 836-2671

Fig. (2)



XBL 836-2668

Fig. (3)

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