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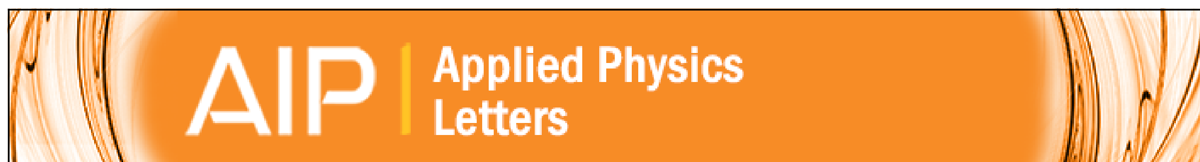

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Citation: Applied Physics Letters **44**, 116 (1984); doi: 10.1063/1.94569
View online: http://dx.doi.org/10.1063/1.94569
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Doping effects in off-stoichiometric glow discharge amorphous silicon nitride

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(Received 29 June 1983; accepted for publication 13 October 1983)

The effects of boron and phosphorus doping on the electrical properties of a-SiN_x:H films are studied. The material is obtained by the glow discharge of SiH_4 and N_2 mixtures. It is found that for Si-rich materials boron doping produces large conductivity variations while phosphorus appears to be a much less efficient dopant. A phenomenological explanation is given assuming that phosphorus prefers to form bonds in accordance with its own valence configuration; i.e., it will go substitutionally to threefold coordinated N sites. Experimental evidence of such behavior obtained from published IR transmission measurements confirms this assumption.

PACS numbers: 73.60.Fw, 78.65.Jd, 81.40.Rs, 61.70.Tm

In 1976, Spear and Le Comber demonstrated that glow discharge (GD) hydrogenated amorphous silicon (a-Si:H) can be effectively doped.[1] Good transport properties combined with a high absorption coefficient in the visible part of the solar spectrum made this material a potentially useful semiconductor for photovoltaic applications and 5% conversion efficiency solar cells were soon produced. Recent work shows that higher efficiencies can be obtained with heterostructures using a-Si:H as the active absorber layer and a wide gap material for the window side junction of a *pin* solar cell. Amorphous silicon carbon alloy (B doped) allowed the Osaka group to attain 8% conversion efficiencies.[2] Attempts to develop new window materials have been made with different amorphous alloys such as a-SiN_x:H and a-SiO_x:H. Knights *et al.* found optical gap changes for different oxygen contents in the a-SiO_x:H network.[3] Anderson and Spear were able to produce off-stoichiometric amorphous silicon nitride with an optical gap varying between 2.5 and 5 eV.[4] However, their material did not possess good semiconducting properties. Recently Kurata *et al.* prepared variable band-gap a-SiN_x:H by plasma decomposition of SiH_4 and NH_3 mixtures.[5] As SiH_4 and NH_3 have similar dissociation energies the nitrogen content in the sample is closely related to the NH_3/SiH_4 gaseous ratio used in the reactor chamber. Doping experiments using B_2H_6 and PH_3 were also performed. Large conductivity variations were measured with the former dopant while phosphorus appeared to produce a much less important effect.

In this letter we present results on the optical and electrical properties of off-stoichiometric silicon nitride compounds. Samples were prepared by the simultaneous plasma decompositon of SiH_4/N_2 gaseous mixtrues in a capacitively coupled glow discharge system, similar to the one described by Knights.[6,7] Combined SiH_4 and N_2 flow varied between 280 and 360 sccm. In all experiments the substrate temperature was kept constant at 280 °C. Deposition pressure was maintained between 0.6 and 0.8 Torr. Peak to peak voltage was continuously monitored and a dc bias of $-$ 100 V was applied to the substrate, all the samples being of the anodic type. The power delivered by the 10-MHz generator was measured by a rf power meter set as close as possible to the input electrode. The growth rate of 1.5 Å/s for the reported samples. A decreasing growth rate with rf power was observed indicating a competitive phenomenon between film formation and film etching. Argon diluted phosphine and diborane, as well as pure silane and nitrogen of electronic grade, were used. 7059 Corning glass substrates were used in all cases. Optical measurements were made with a Zeiss DMC 25 spectrophotometer. The film thickness of the samples used to obtain the conductivity data was 1 μm. Sample thicknesses were deduced from optical measurements and confirmed by mechanical profilometer techniques. Dark conductivity as a function of temperature, for intrinsic and doped material, was measured in an inert chamber. Coplanar 10-mm-long aluminum strips 0.5 mm apart were evaporated on the samples. Excellent ohmic behavior was observed in the 10–50-V polarization range. Conductivity measurements were performed within this bias range.

Brenzikofer and Chambouleyron have shown that the optical gap of glow discharge a-SiN_x:H samples prepared from SiH_4 and N_2 mixtures shifts with increasing rf power densities and depends on silane to nitrogen gaseous ratio.[8] Optical band gap is here defined as the extrapolated energy value of the high absorption portion of the $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot. Highly nitrogen diluted silane allows scanning an optical band gap that goes from 1.8 to more than 5 eV. Why does an increasing rf power change the N/Si ratio in the sample? A phenomenological explanation follows.[8] The dissociation energy of the nitrogen is 2 to 3 times larger than that of the silane molecule. At low rf power densities the plasma will essentially break silane molecules and the material will not differ much from a-Si:H. Higher power densities produce more and more nitrogen radicals in the plasma increasing the number of nitrogen atoms incorporated into the network. The concentration of active nitrogen in the plasma is then related to rf power density. Thus the composition of the sample depends on both rf power density and SiH_4/N_2 gaseous ratio. This phenomenological picture was confirmed by recent IR measurements.[9]

Figure 1 shows the $(\alpha h\nu)^{1/2}$ vs $h\nu$ curves of a series of samples prepared using identical conditions except rf power density. It can be seen that for a fixed silane dilution ($SiH_4/N_2 \sim 33\%$) the absorption edge shifts towards higher energies with increasing rf power density.

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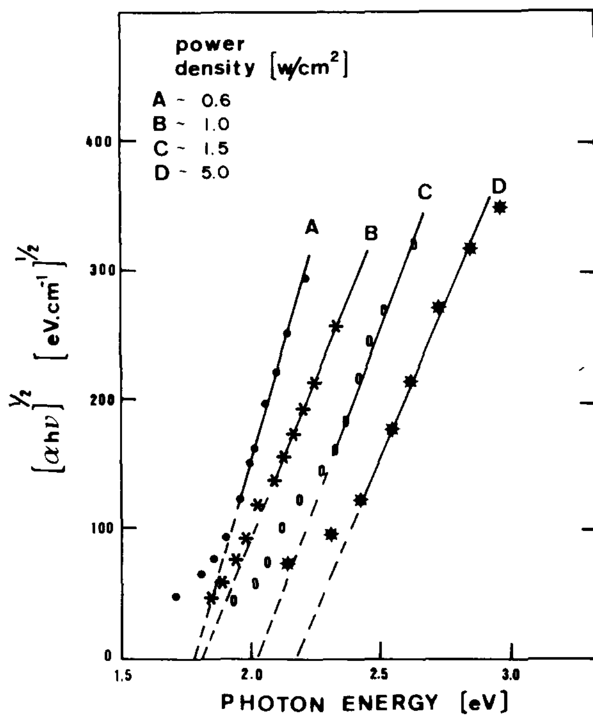

FIG. 1. $(\alpha h\nu)^{1/2}$ vs photon energy for different a-Si_xN_{1-x}:H layers obtained from the GD of a SiH_4 and N_2 mixture of fixed composition $(SiH_4/N_2) = 0.33$. All samples are nonintentionally doped and rf power density is indicated on each curve.

The particular growth conditions under which we have chosen to investigate doping effects produce an alloy having an extrapolated optical gap of ~2.0 eV (curve C).

The extrapolated room-temperature conductivity and the correspoding activation energies versus B_2H_6/SiH_4 and PH_3/SiH_4 gaseous ratio are shown in Figs. 2(a) and 2(b). The former shows that the material is slightly n-type when defect controlled. Minute amounts of diborane decrease the conductivity and increase the activation energy indicating that Fermi level is pushed downwards towards midgap. Diborane dilutions higher than $B_2H_6/SiH_4 \sim 10^{-3}$ lead to a continuous conductivity increase of several orders of magnitude. For a dilution ratio of $B_2H_6/SiH_4 \sim 1.2\%$ the activation energy drops to 0.53 eV [Fig. 2(b)]. On the right side of the figure results corresponding to phosphine doping are plotted. Conductivity and activation energy variations are much less impressive indicating that, concerning transport properties, P is a less efficient dopant than B. In fact, these results are similar to those obtained by Kurata *et al.* on off-stoichiometic silicon nitride produced by plasma decomposition of SiH_4/NH_3 gaseous mixtrues.[5] We believe that large differences in doping efficiencies are related to the chemical structure of the material and not to the particular method used to prepare the samples.

We have also performed IR absorption experiments on intrinsic samples and strong Si–H and Si–N absorption bonds were observed. The integrated areas of the former band indicate a hydrogen content of ~17 at. %.[9] Due to the uncertain absorption strength constant for Si–N band we have not yet a reliable experimental value for nitrogen concentration. However, from theoretical plots of N/Si structures versus refractive index we estimate the nitrogen con-

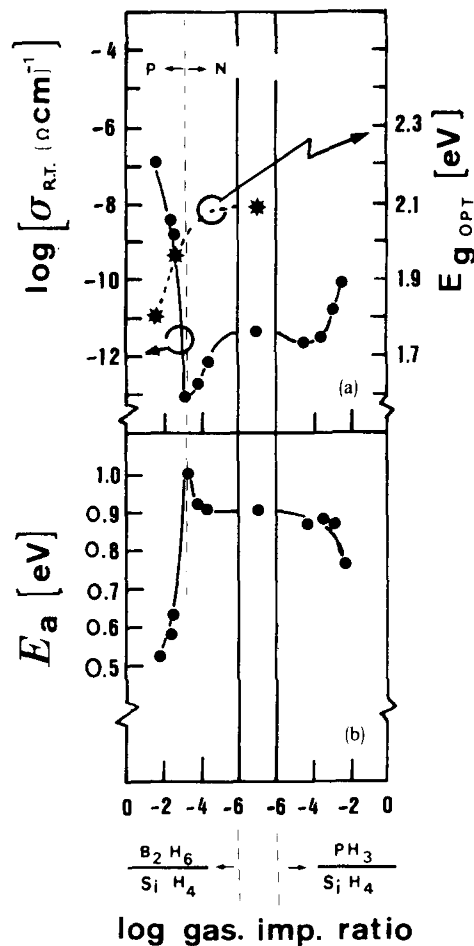

FIG. 2. (a) Room-temperature conductivity vs gaseous doping mixture for samples grown under conditions identical of those of curve C, Fig. 1. The effect of optical gap shrinking due to boron doping is also indicated. (b) Dark conductivity activation energies vs gaseous doping mixture. It is found experimentally that the conductivity varies with temperature according to $\sigma = \sigma_0 \exp(-E_a/kT)$ in the 300–500-K temperature range.

tent of our samples to be ~20–30 at. %.[10]

What follows is an attempt to explain the experimental results. Off-stoichiometric amorphous silicon nitrides are midway materials between a-Si:H and a-Si_3N_4:H. This can be interpreted essentially in two ways: (1) a microcluster model where small a-Si_3N_4 units are randomly distributed in the network; (2) a more uniformly perturbed network where nitrogen is included in a way that clustering is not preferred.

Presently we cannot conclusively determine which of the above models is more appropriate and thus more experiments are needed. However, one can say that the process which decreases the network energy will dominate the growth mechanism giving either a homogeneouslike matrix or a two-phase material. Furthermore, in GD off-stoichiometric silicon nitride the presence of large amounts of hydrogen contributes to network relaxation.

It is by now well accepted that amorphous semiconductors might not be homogeneous random networks but instead might possess structural and/or compositional microscopical inhomogeneities. If these inhomogeneities can grow, formation of clusters will depend on how nitrogen atoms interact with the network. They might prefer to accommodate, in a strain-free region instead of in the vicinity

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of an already existing N–Si bond giving a more uniformly perturbed network.

Chemical vapor and glow discharge deposited silicon nitrides are amorphous. Radial distribution function experiments show that local configurations are very similar to those in stoichiometric polytype β-Si_3N_4 with planar bonded N and tetrahedral bonded Si.[11] This structure is consistent with sp^3 silicon hybrid orbitals while N bonding has been explained in terms of a linear combination of p orbitals, the planar geometry being given by a strong repulsion of nonbonded Si atoms. According to these calculations nitrogen electrons do not participate in bonding and the top of the valence band is given by nonbonding N-p_z^2 electrons.[12]

An alternative explanation could be a nitrogen sp^2 hybridization and a N p_z^2 nonbonding orbital, the repulsion between lone pairs being responsible for the hexagonal close packed structure.[13] Both explanations lead to the interpretation of silicon nitride as a lone pair semiconductor.

We now consider the differences in boron and phosphorus doping effects. It was once believed that amorphous semiconductors could not be doped. Not being constrained by a crystalline matrix the impurity atom would form bonds in accordance with its own valency. It is now well known that this is not necessarily so. In the a-Si:H network impurities like B and P are partially incorporated in substitutional sites. Nevertheless, the problem concerning doping efficiencies has not received a definitive answer and is probably related to network topology and partial microcrystallization. Additional information to our problem is given by the IR transmission measurements made by Kurata *et al.*[5] These researchers studied B and P-doped off-stoichiometric a-SiN_x:H samples. In B-doped materials they found an increasing amount of B–N bonds with increasing boron doping in detriment of N–Si bonds. On the other hand P–doped films do not exhibit a P–N absorption band, as one might expect if P replaced Si atoms in the network.

Electrical and optical measurements and the above-mentioned results lead us to conclude that (1) boron is largely incorporated in a fourfold bonded configuration and acts as an acceptor impurity in the silicon structure, (2) phosphorus prefers to form bonds in accordance with its own valence configuration. It will prefer N sites and will not produce an extra electron in the conduction band. However, small conductivity changes are measured indicating that some phosphorus atoms are fourfold bonded.

We believe that the behavior of boron and phosphorus is strongly related to material composition. In silicon-rich samples the conductivity variations would be larger for both dopants. As the composition approaches the silicon nitride stoichiometry, doping becomes less and less effective. A greater availability of threefold coordinated sites increases phosphorus probability of coordination according to its valence configuration. On the other hand, fourfold bonded boron will have less opportunities of being surrounded by Si atoms.

The low phosphorus doping efficiency could also be related to a high density of gap states coming from structural defects. However, Fig. 1 shows steep straight lines on the high absorption part of the curves. By extrapolation a well defined optical gap is obtained indicating low density of states in the gap. Furthemrore, absorption coefficients deduced from photoconductivity measurements indicate an exponential shape down to a few cm^{-1}.

Finally, although samples prepared from SiH_4/NH_3 and SiH_4/N_2 processes might have a different H content we believe that the H incorporation produces a minor effect as far as gap widening is concerned.

The authors are indebted to Professor C. Gonçalves da Silva (UNICAMP) for fruitful discussions. They also acknowledge clarifying comments from Professor M. Cardona (Max Planck Institute, Stuttgart), Dr. S. Pantelides (IBM, Yorktown Heights), and Professor W. Paul (Harvard University, Cambridge).

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