

07.8-9 THE STRUCTURE OF BORON- AND PHOSPHORUS-DOPED AMORPHOUS SILICON THIN FILMS. By D.R. McKenzie, D.J.H. Cockayne*, Z. Liu, D.M. Dwyer* and S.A. Song*, School of Physics and *Electron Microscope Unit, University of Sydney, Australia.

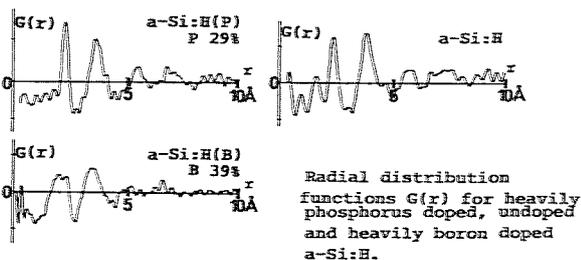
The aim of this diffraction study is to determine whether there is a pronounced difference in the manner in which P and B are incorporated into the amorphous silicon network. Self-supporting specimens, 50nm thick, of pure and doped a-Si:H were prepared by glow discharge decomposition of silane with phosphine and diborane.

The electron diffraction intensity $I(s)$ was collected in a Philips EM430 electron microscope operating at 300kV, using an electron energy loss spectrometer to remove inelastically scattered electrons. The intensity was processed (A. Sproul, D.R. McKenzie and D.J.H. Cockayne. Phil. Mag. B 54, 113 (1986)) to give the radial distribution function

$$G(r) = \frac{2}{\pi} \int_0^\infty \frac{(I(s) - Nf^2)}{Nf^2} s \sin sr ds$$

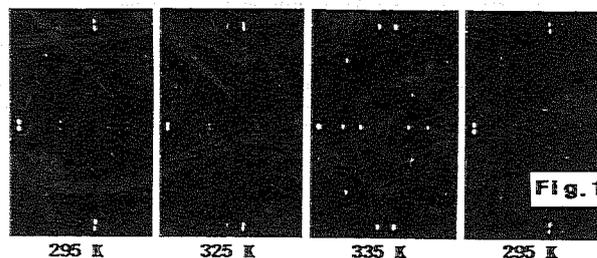
The $G(r)$ for heavily phosphorus doped a-Si:H (29% P as determined by EDS) and for heavily boron doped a-Si:H (39% B as determined by EELS) are shown in the figure, together with the $G(r)$ for undoped a-Si:H. There are obvious differences between the effects of the dopants. In the case of boron, two adjacent maxima in $G(r)$ occur at $r=1.90 \pm 0.05 \text{ \AA}$ and $2.37 \pm 0.02 \text{ \AA}$. Detailed analysis shows that these can be interpreted as a superposition of peaks close to the neighbouring atoms in the boron icosahedron (1.80 \AA) (L.S. Palatnik, A.A. Kozma and A.A. Mechitailo. Sov. Phys. Crystallogr. 28 73 (1983)) and to the Si-Si distance in the amorphous silicon (2.37 \AA). In the case of phosphorus, the first maximum in $G(r)$ occurs at $r=2.29 \pm 0.02 \text{ \AA}$, which is significantly shorter than the first maximum of undoped a-Si:H at $2.37 \pm 0.02 \text{ \AA}$. There is no broadening of this peak, and hence no evidence of Si-Si bonding at the undoped distance of 2.37 \AA . The maximum at 2.29 \AA probably corresponds to the Si-P distance. The P-P distance is approximately 2.25 \AA in elemental phosphorus (M.W. Greenwood and A. Earnshaw. 'Chemistry of the Elements', Pergamon Press, Oxford, 1984, p. 554). The compound Si_3P is known (Von G. Fritz and H.O. Berkenhoff. Z. Anorg. Allg. Chem. 289, 250 (1957)) as an amorphous solid, formed by heating phosphine and silane together. It is quite likely that the heavily P-doped specimen contains this compound as the principal constituent. Since the peak is narrow we deduce that this compound contains mainly Si-P bonds and few Si-Si or P-P bonds.

This study indicates that heavily B-doped a-Si:H contains significant amounts of B in the form of the stable boron icosahedron. As a consequence B is not uniformly distributed throughout the network. On the other hand, in heavily P-doped a-Si:H, phosphorus remains bonded to silicon in a modified network.



07.9-1 THE ORTHORHOMBIC/MONOCLINIC SYMMETRY CHANGE IN SINGLE CRYSTALS OF ZEOLITE ZSM-5. By H. van Koningsveld, H. van Bekkum and J.C. Jansen, Laboratories of Applied Physics and Organic Chemistry, Delft University of Technology, Lorentzweg 1, 2628 CJ Delft, The Netherlands.

The structure of a large ($200 \times 150 \times 250 \text{ \mu m}$) orthorhombic (Pnma) single crystal of ZSM-5, including the template ion (tetrapropylammonium) is presented. Contrary to literature data the propyl-N-propyl fragments pointing into the sinusoidal and straight channel both have CNCC torsion angles around 60° . The template ion occupies four positions in a disordered way: two around m and another two around a 'pseudo- m ' perpendicular to m . X-ray photographs are shown of crystals of ZSM-5 (Si/Al ≈ 300) in the as-synthesized and calcined form. Calcination changes the symmetry of the crystals to monoclinic. Fig. 1 shows details of rotation photographs around b of a calcined crystal of ZSM-5 at different temperatures. The reversible monoclinic/orthorhombic transition (no hysteresis; transition temperature ≈ 330



K), previously studied with XRD and Silicon NMR on powder samples of ZSM-5, is clearly observed. The orthorhombic single crystal changes into a monoclinic multi-domain aggregate when the temperature is lowered. The domains have common a and c axes while, alternately, $\alpha \approx 90.5^\circ$ or 89.5° . The deviation of α from 90° is caused by a change in the direction of b in the (100) plane. The change in the direction of b can be realized by a shear of the (010) pentasil layers along [001], induced by a distortion or displacement of the T_4 and T_5 rings interconnecting the layers (Fig. 2). Both shear deformations have equal probability leading to a twin domain structure given in Figure 3. The space group of the monoclinic phase most probably is $P2_1/n.1.1$.

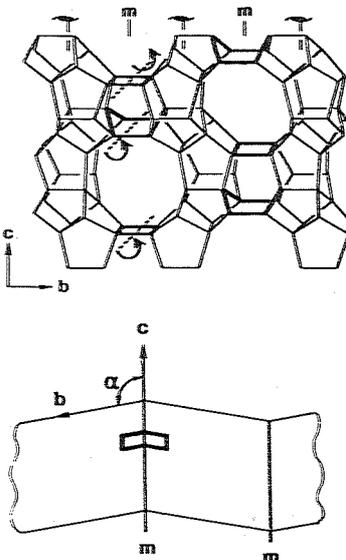


Fig. 2. (100)-Pentasil layer showing T_4 and T_5 rings heavy dark. The as-synthesized ZSM-5 framework is completed by linking neighbouring (100) layers via symmetry centers.

Fig. 3. Part of the twin domain structure in a monoclinic twinned (calcined) crystal of ZSM-5 seen along [100]. Deformed (100) pentasil layers at both sides of m are heavy dark outlined.