20-Industrial Crystallography

MS-20.31.07 THE USE OF DYNAMIC AND STRUCTURAL CRYSTALLOGRAPHIC TECHNIQUES TO STUDY THE SYNTHESIS OF SULFONIA. By Xavier Terrilles, Industrial Materials Group, Crystallography Dept. Birxbeck College (University of London), Male Street, LONDON W1K 6XX, UK.

There is a considerable research effort in the engineering of strontium ceramics. This is due to its current applications and potential uses in other fields (fuel cells for instance). The strontium-carbonate hexahydrate part of a collaboration project between industry and University and illustrate how the facilities and analytical techniques only available from its science institutes, can be used in the solution of narrowly defined technological problems.

In this work we present our conclusions to the understanding of how the oxide crystallization from the hydrous precursors takes place, and how the transition, at higher temperatures, between the tetragonal and monoclinic phases occurs. In particular, we have focused our attention on the influence of the preparation pH of the hydrate. In order to achieve this, we have used real time analytical techniques, such as time-resolved Synchrotron Energy Dispersive Diffraction and Neutron Thermo-Diffactometry (NTD).

As a complement to determine the local strontium hydration structure, synchrotron X-ray powder diffraction was used at room temperatures and under applied as well. Different thermal treatments (heating and cooling ramps and dwelling times) were applied to various samples in order to examine their influence on the crystallization rate and the tetragonal-monoclinic transition temperature. The influence of the preparation pH on the crystallinity from the hydrate has also been determined using conventional 2θ-2θ and neutron diffraction techniques and Energy dispersive diffraction.

The influence of thermal treatment on the tetragonal-monoclinic transition temperature is more complicated but clear trends of behaviour have emerged from the experimental data. Briefly, the higher the dwelling temperature and time, the higher is the transition temperature. On the other hand, the specimens prepared at low pH are more sensitive to heat treatment. Another observation reported by other authors concerning the relation between crystallinity and the tetragonal-monoclinic transformation temperature has also been confirmed here. Regarding the crystallisation from the hydrate, it seems to occur at least in three stages. A careful analysis of the NTD integrated profiles, by fitting to a tentative theoretical model suggests that the first stage is related to the removal of terminal OH- (H2O) 2D-groups of the hydrate, whereas inner-water removal and exfoliation (two hydrate bonds reduced to one calcium and free water) are involved in the two subsequent stages.

MS-20.01.08 STRUCTURAL FEATURES OF POROUS SILICON WITH VISIBLE PHOTOLUMINESCENCE. By Osamu Kittono*, Enoki Takekoto and Yukio Nakamura., Department of Metallurgy, Tokyo Institute of Technology, 2-12-1 Oh-okayama, Meguro-ku, Tokyo 152, Japan.

It has been reported that porous silicon (PS) has wirylike (or columnar) structures of less than 10nm in diameter and that the effective photoluminescence is due to a quantum size effect resulting from such isolated fine rods. The size and morphology of such PS, however, is strongly related to the dopant type and content ( or resistivity ) as well as preparation conditions such as current density and HF concentration ( Sugiya and O.Kittono, J. Cryst. Growth, 1989. 105, 156-163 ). In order to understand the mechanism of photoluminescence, it is first necessary to examine the photoluminescence of porous Si in relation to the real microstructure of PS. Therefore, in this study the microstructure, morphology, size, lattice expansion and crystallinity of PS's, which were formed on p-type and n-type degenerate Si(100) substrates of less than 0.02 cm resistivity, were studied by means of high resolution scanning microscopy, X-ray micro-crystal diffractometry, high resolution electron microscopy. Amorphization was carried out with current densities ranging from 10 to 300 mA/cm² in a constant electrolyte of HF:CH3OH:H2O=1:1:2 with the reaction time from 15 to 30 min. All the n-type PS's were prepared under illumination by a He-Cd laser beam (325nm) luminescent color varied from yellow to orange according to preparation conditions. The main results are as follows: (1) p-type PS: PS showed color changes from bluish-gray to dark golden brown with increasing the porosity. When PS was prepared above 250 mA/cm², the lattice distortion decreased and the crystallinity was considerably worse than that of the substrate, and visible luminescence was appreciated. PS, which is composed of large pores, showed slightly larger lattice distortions than PS, composed of small pores: the smaller in diameter the remaining Si rods were, the larger the lattice distortion was. This was also confirmed by investigating X-ray intensity distribution around the reciprocal lattice point for PS, indicating that the lattice relaxation easily takes place with decreasing the small radius of the remaining Si rods. The remaining Si rods were found to be composed of particulate like structure of various sizes from several nm to several tens of nm ( a kind of mosaic structure), probably as a result of stress relaxation of the remaining Si rods in PS layer. (2) n-type PS: Characteristic of the crystallinity and morphology of PS were quite different from those of p-type PS. Illumination was found to be very effective in producing PS on n-type Si substrates. From structural observations of PS's prepared by varying the reaction time in a range from 1 to 15 min., it was revealed that the microstructure of PS, when produced for a long reaction time, was composed of mainly three layers which exhibit different pore morphology: a spongy structure, composed of fine Si particles. In the upper region near the surface, a dendritic one in the middle region, and a cylindrical one in the lower region near the interface between PS and Si substrate. The depth profiles measured by a heavy-ion ERD (Elastic Recoil Detection) spectrometer for PS's emitting strong photoluminescence showed that hydrogen atoms were densely concentrated near the upper surface of the PS layer, even after being annealed at 950°C in dry nitrogen ambient. This result suggests that the origin of the photoluminescence is related to the existence of hydrogen atoms near the PS surfaces.

PS-20.01.09 PHASE IDENTIFICATION IN STEEL BY ELECTRON MICROSCOPY

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The advantage of electron microscopy over x-ray is the ability to relate the phase to the morphology and chemistry in a very small area in steel. The composition of a given phase varies depending upon the alloy composition and thermal mechanical treatment. Therefore, electron diffraction is the only reliable way to identify a phase. Because of the three dimensional information of the convergent beam electron diffraction (CBED) only one pattern from high-symmetry zone axis may be needed for phase identification (J.W.Steed & R.Vance, J. Appl. Cryos., 1984, 16, 137-157). Across the entire range of equivalent CBED patterns, it is important to examine the electron microscopy of the recognizable ZL0 as well. The other one may be obtained in the ZL0. The contrast is not as intense as in the ZL0 due to the extinction of the 3000, 6000, 9000 type reflections in the ZL0, (Fig. 2). Meanwhile, M9 and M10 can readily be distinguished. In the ZL0 one zone axis of (400) zone axes, which are four reflections in the ZL0, are shown in Figs. 3a and 3b. The essential point is that the ZL0 are very similar for all three patterns (Note that the camera lengths are different in Figs. 3a-3c). There are no