Final Technical Report
"Diffraction Studies of Glasses, Liquids and Nanoclusters"
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A. The amorphous structure factor of thin SiO₂/Si(001)

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Amorphous SiO₂ is classically understood as a continuous random network forming glass. Typically amorphous materials possess no translational symmetry, which is the signature of a crystal. Our interest in investigating SiO₂, grown as a thin film (100, 500 Å) on Si(001), is to observe how this particular amorphous phase is able to couple to the crystalline substrate and reflect a peculiar degree of order.

The basic structural unit in vitreous SiO₂, Fig. 1, is a tetrahedron of oxygen atoms surrounding a silicon atom. Correlations of the distances highlighted in Fig. 1 give rise to a prominent feature in the bulk structure factor, known as the first sharp diffraction peak (FSDP), which appears at $Q \approx 1.5 \text{ Å}^{-1}$, Fig. 1. We take advantage of the high flux available at the Advanced Photon Source (APS) to study, in grazing incidence diffraction (GID) geometry, the amorphous structure factor of thin SiO₂. Tetrahedral units are expected to accommodate, over the crystalline silicon template, and thus yield changes in position and intensity of the FSDP. Fig. 2 shows that effect in a reciprocal space map, $\{HK0\}$, scaled in the Si crystal notation (100 Å film).

The FSDP (Fig. 2, measured at an incident angle of 0.05° , i.e., below the 0.08° critical angle for total external reflection) traces a semi-ring, with enhanced intensity at the Si(110) positions (whose reflections are forbidden by symmetry), i.e. at $Q \approx 1.6 \text{ Å}^{-1}$.

The remaining trace of the FSDP, with reduced intensity, appears at $Q \approx 1.4 \text{ Å}^{-1}$. An independent measurement, solely rotating the sample in ϕ , around its normal, collects the intensity along the radius described by the Si(110) position in reciprocal space.

The depth dependence was investigated through analyzing a 500 Å SiO₂ film. A position sensitive detector (oriented normal to the sample surface) aided in simultaneously collecting data from within the first 100 Å depth, Fig. 4, as well as down to the interface with bulk Si, Fig. 5. To observe the structure factor

thickness and the growth temperature. A thinner film would be expected to undergo a higher compression, and a larger variation in the FSDP position would be a reasonable consequence.

$Si[110]$, the directions of FSDP intensity enhancement. Also, in agreement with the CTR modeling, the density of crystallites is expected to diminish exponentially towards the film surface, a fact essential in fitting the CTR oscillations.

B. Off-edge, and near Se-K and Hg-L edge, measurements of HgSe nano-clusters in Nd-Y zeolites

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Zeolites provide a very stable aluminosilicate framework with well defined pore sizes. Additionally they are prone to absorb molecular species. Molecular clusters of semiconductors could thus be constrained to grow within zeolite pores and vary their bulk behavior. Ekimov and Onushchenko (A. I. Ekimov and A. Onushchenko, Sov. Phys. Semicond **16**, 772 (1982)) observed how the absorption spectra of small

modulation, the FSDP was registered at each azimuthal position (ϕ), out of successive radial scans along a 180° ϕ -range. From Fig. 4, the modulation in the thin film top-most region is statistically non-existent, while close to the substrate (Fig. 5) is clearly four-fold. At $\phi \approx 110^\circ$ we have the $Si\langle\bar{1}10\rangle$ direction, and at $\phi \approx 20^\circ$ the $Si\langle110\rangle$, these being positions with maximum intensity located at $Q \approx 1.485 \text{ \AA}^{-1}$. The minima, in Fig. 5, are at $Q \approx 1.455 \text{ \AA}^{-1}$. These variations of the FSDP position represent an expansion of the structural units of SiO_2 that average 2% when compared to the standard vitreous silica FSDP; a smaller variation than in the 100 $\text{\AA}$ film, 8 %. Note that there is a correlation between the film

Along with other groups, we have also found, in the APS experiments, a crystalline peak at $L \approx 1.4 \text{ \AA}^{-1}$ (accompanied by its Laue oscillations, with a period corresponding to the film thickness) in the Si 11L crystal truncation rod (CTR). We reconcile the crystalline peak and the FSDP depth-dependent modulation through the inclusion of a sparsely distributed, and distorted, crystalline phase of SiO_2 , (pseudo-coesite (PC), Fig. 6) embedded within the amorphous film. One of the PC axes (along $Si\langle001\rangle$) closely matches the crystalline peak position observed in the CTR, while another axis would be aligned in the

particles of CuCl differed from its bulk counterpart. This phenomenon is explained as a consequence of the space quantization of the bound electron-hole pair. When the individual clusters of the semiconductor

are about the size of the Bohr radius, associated to the electron-hole pair, quantum effects arise that alter the bulk optical and electronic properties.

We are using a II-VI compound semiconductor, mercury-selenide (HgSe) and Na-Y zeolite (faujasite, Fig. a) as a template. Through ionic exchange the sodium (Na), which actually resides in the pores of the aluminosilicate framework, is substituted by neodymium (Nd). This last element, due to its coordination number, is able to substitute for up to three Na atoms, increasing the space

available for storage of the HgSe clusters. With pore sizes of the order of 10^{-9} m, a unit cell of HgSe (cubic, $a = 6.08$ Å), can, in principle, fit within the sodalite (the largest pore) cage of the zeolite. But the shape of the potential given by the zeolite framework will, most likely, tailor the structure of the HgSe compound.

The analysis of the cluster structure is performed by X-ray diffraction in the near absorption edge and off-edge of Hg and Se, at a synchrotron source (X7A, National Synchrotron Light Source, Brookhaven, N.Y.). Our strategy consists of utilizing differential scattering measurements in the manner of Nichols et al. (J. Appl. Cryst., 18, 8 (1985)). Figure b shows an energy-versus-dispersive-terms of the scattering factor, indicating the energies used.

Presently there are also some hydration problems that we are addressing. Zeolites are very hydrophilic, and although the samples are kept inside a holder that provides encapsulation, some moisture from the environment permeated into the pores.

Some of our first data sets present the clear changes in peak intensity, that HgSe clusters, induce in the Nd-Y zeolite through distortion of its structure. Particularly outstanding are the intensity variations in

the Nd-Y zeolite (400), (331), (422) and (611) positions in reciprocal space. Off-edge ($\lambda = 1.198$ Å), the peaks mentioned previously (Fig. c), show a gradual intensity reduction. The sample with cluster

concentration Hg₂₁Se₃₂, exhibits a peak at about $L = 1.778 \text{ \AA}^{-1}$ that does not appear in the Nd-Y zeolite without clusters, and that with Hg₂₁Se₁₆ cluster concentration. at 15 eV above ($\lambda = 0.9865 \text{ \AA}$), the Se-K edge (Fig. d), similar features can be observed, together with a prominent peak mismatch between $3.4 \text{ \AA}^{-1}$ and $3.5 \text{ \AA}^{-1}$ (Fig. e). Figure f contains the results obtained 20 eV below ($\lambda = 0.8723 \text{ \AA}$) the Hg-L edge.

In addition to the Nd-Y zeolite, we will also carry out experiments using LTL and AlPO₄ zeolites. These last two have a tubular pore, unlike the first one (with a sphere-like pore). One advantage of zeolite hosts is the variety of pore sizes and

shapes, which permit a study of different degrees of variation in the nano-cluster properties.

It is relevant to note the singular change in the background, as a function of energy. This is probably due to orientational disorder of the HgSe clusters within the zeolite cages. Often it happens that the defects

are responsible for the properties observed in certain materials; hence the importance in understanding them.

Further measurements using a pair distribution function (PDF) technique are under way also at X7A, in Brookhaven and are also planned for the APS/Anl, where the intensity is greater and can be extended to higher Q. These experiments will disclose structural information on the defects and disorder present in the system after inclusion of the HgSe clusters. The PDF formalism reflects the structure of the material through Fourier transforming the powder pattern of an extended

reciprocal space data set. Characteristic peaks in the PDF will be indicative of distances in pairs of atoms that, through modeling, will reveal the local structure. The empty zeolite will be used as a reference.

Student and Post-Doctoral Progress

Miguel Castro-Colin, Ph.D. received December 2003, on "X-ray diffraction studies of $\text{SiO}_2/\text{Si}(001)$ "; currently continuing as Post-doctoral Fellow.

Milinda Abeykoon, Ph.D. in progress on "Studies of HgSe nanoclusters in Nd-Y and tubular zeolites".

Publications

M. Castro-Colin, W. Donner, S. C. Moss, Z. Islam, S. K. Sinha, R. Nemanich, H. T. Metzger, P. Boesecke, T. Shuelli. "Synchrotron X-ray studies of vitreous SiO_2 over $\text{Si}(001)$. Part I: Anisotropic glass contribution". Phys. Rev. B, 71 (4) 15 January 2005, pp. 045310.

M. Castro-Colin, W. Donner, S. C. Moss, Z. Islam, S. K. Sinha, R. Nemanich, "Synchrotron X-ray studies of vitreous SiO_2 over $\text{Si}(001)$. Part II: Crystalline contribution". Phys. Rev. B, 71 (4) 15 January 2005, pp. 045311.

Presentations

S. C. Moss, "Synchrotron Grazing Incidence and Truncation Rod Studies of Thin Vitreous SiO_2 over $\text{Si}(001)$ ", Journees Soleil 3emes Rencontres Interdisciplinaires, Orleans, France, Mar. 31-April 1, 2003.

S. C. Moss, "Synchrotron Grazing Incidence and Truncation Rod Studies of Thin Vitreous SiO_2 over $\text{Si}(001)$ ", National Institute of Standards and Technology, Washington, DC, April 22, 2003

S. C. Moss, "Synchrotron Grazing Incidence and Truncation Rod Studies of Thin Vitreous SiO_2 over $\text{Si}(001)$ ", Max Planck Institute for Solid State Physics, Stuttgart, Germany, Summer 2003.

S. C. Moss, "X-ray Study of Thin SiO_2 over $\text{Si}(001)$ ", Retirement Fest for Professor Roberto Colella, Purdue University, Nov. 14-16, 2003.

W. Donner, M. Castro-Colin, S. C. Moss, Z. Islam, S. K. Sinha, R. Nemanich, H. T. Metzger, P. Boesecke and T. Schuelli, "Not so amorphous silicon dioxide films on silicon," to be presented at Deutschen Physikalischen Gesellschaft (German Physical Society), Berlin, March 4-9, 2005

M. Castro-Colin, W. Donner, S. C. Moss, R. J. Nemanich, Z. Islam, S. K. Sinha "The structure of vitreous SiO₂ over Si(001)", Symposium on Scattering from Disordered and Defective Materials, Houston, TX, October 2, 2004.

M. Castro-Colin, W. Donner, S. C. Moss, R. J. Nemanich, Z. Islam, S. K. Sinha. "Crystal truncation rod fitting of thin SiO₂ on Si(001) system", 2003 Texas Section Joint Fall Meeting of the APS, Lubbock, TX, October 23-25, 2003.

M. Castro-Colin, W. Donner, and S. C. Moss. "X-ray diffraction studies of thin SiO₂ on Si(001)", 2003 Physical Electronics Conference, Ithaca, NY, June 16-18, 2003.

M. Castro-Colin, W. Donner, S. C. Moss, R. J. Nemanich, Z. Islam, S. K. Sinha. "Amorphous structure modulation of thin SiO₂/Si(001), APS March Meeting 2003, Austin, TX, March 3-7, 2003.

M. Castro-Colin (student award winner), W. Donner, S. C. Moss, R. J. Nemanich, Z. Islam, S. K. Sinha, "Grazing-incidence measurement of amorphous structure modulation in thin film SiO₂ on Si(001)". 2002 Texas Section Joint Fall Meeting of the APS, Brownsville, TX, October 10-12, 2002.

M. Castro-Colin (2nd place), "Modulation of the amorphous structure of SiO₂ over Si(001)". 23rd Semiannual TCSAM Student Symposium, Houston, TX, May 2, 2002.