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Structural Characterization of Very Thin Films by Fluorescence-Detected X-Ray Absorption Spectroscopy

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Due to the recent developments in very thin film technology, interests in structural characterization of thin films have rapidly grown. Fluorescence-detected x-ray absorption spectroscopy (XAS) using synchrotron radiation as a light source can be a powerful structural tool in that: (1) the local structure and bonding states of a particular atomic species are obtained thereby allowing a multicomponent systems to be studied, (2) thin films over a wide range in thickness from a few thousand Å down to even a few Å can be probed, (3) because XAS is based on the short range order, disordered systems, e.g. amorphous thin films formed by ion beam implantation or glow discharge, are studied, (4) since surface cleaning or in-situ sample preparation are unnecessary for the x-ray spectrocopy, thin film samples of interest prepared by various epitaxial growth techniques are rutinely characterized.

In this late news, we present the feasibility of fluorescence-detected XAS using the recently built multi-detector system (MDS). The ion-beam-induced structural modification of thin nickel lavers on Si(100) were studied by fluorescence-detected XAS as an example of the application to thin film studies.

Figure 1 illustrates the experimental setup for fluorescence-detected XAS utilyzing x-radiation from 2.5 GeV storage ring at Photon Factory. The x-ray beam line optics featuring a constant beam height double crystal monochlomator and a bent cylindrical mirror provides an intense photon flux of 10^{10} photons/sec with an energy resolution $\Delta E/E \sim 10^{-4}$. For fluorescence-detected XAS experiments, the detector system is required to be versatile with respect to: (1) the dynamic range in photon counting, (2) the detector geometry to cover a wide solid angle, (3) the energy discriminating capabilities if necessary. However, these requirements are difficult to be attained simultaneously and the situation depends on the concentration and matrices, which vary sample by sample. Therefore, to meet these requirements, we have designed and built the MDS which can cover a wide range in fluorescence detection rate with the optimum detection scheme. The detector system consists of three kinds of detector with different characteristics, i.e. (1) plastic scintillation detector for a concentrated system, (2) NaI scintillation detector for a system down to 10^{-4} in atomic fraction, and (3) Si(Li) detector for the most dilute system or very thin film experiments.

The fluorescence extended x-ray absorption fine structure (EXAFS) spectra of thin nickel layers (50-100 Å in thickness) deposited on Si(100) have been measured on the Ni K-edge to estimate the sensitivity of the MDS. The typical signal-to-background (s/b) ratio for 50 Å thick Ni/Si(100) was 5 with the total count rate of 10^5 photons/sec using nine NaI detectors subtending 18% of 4π steradian and the spectra were recorded in 40 minutes with the sufficient statistics. These results imply that *even a monolayer experiment is feasible* with the use of an x-ray filter which further reduces the background and the increase of the incident beam intensity by an order of magnitude.

The formation of nickel silicide by thermal annealing usually takes three forms: Ni_2Si, NiSi, and $NiSi_2$ which grow sequentially from thin nickel layers on Si.[2] In this study, the ion-beam-induced structural modification of thin nickel layers on Si(100) has been investigated by fluorescence EXAFS. Structural studies of this modification using a glancing angle x-ray diffraction have been hindered because of the abscence of long range order.

Figure 2 illustrates the Ni K-edge absorption spectrum,(a) and the extracted EXAFS oscillations, (b) for 300 Å thick Ni/Si(100) after the argon ion bombardment at 100 keV (Ts=100°C,Nd=3 x $10^{16}/cm^2$). Since the scattering amplitude of nickel has a maximum at a photoelectron wave vector k of 6-7 $Å^{-1}$ and extends a large k of 15 $Å^{-1}$ in contrast with that of low-z element such as silicon which peaks at a small k and falls off sharply with the increase of k, it is readily concluded from Fig. 2b that silicon atoms are the nearest neighbors of nickel species. The Fourier transform further confirmed that the Ni-Si bonds are located at 2.3 Å. There have been observed no Ni- Ni bonds in the vicinity of the first nearest Ni-Si bonds ruling out the possibility of nickel island formation or Ni- rich silicide. Because of a remarkable similarity in the short range order between this disordered phase and that of Si-rich silicide, $NiSi_2$, one may attempt to attribute this phase to the amorphous $NiSi_2$. However, the drastic change in the short range order has been observed for Ni/Si(100) which was ion beam bombarded at substrate temperatures above 400°C. This phase is crystalline and has the similar radial distribution with that of Ni/Si(100) annealed at 400°C which is identified as Ni-rich silicide Ni_2Si by a glancing x-ray diffraction experiment.

These results imply that amorphous Si-rich silicide is formed by the ion beam bombardment below 200°C while Ni-rich crystalline silicide Ni_2Si grows above 400°C. There are also possibilities that nickel atoms are knocked on into Si lattice and take interstitial voids. Details on the structure modification will appear elsewhere. These results are still preliminary. However, they are ample to demonstrate the usefullness of fluorescence EXAFS as a structural tool for thin films without the long range order. In this late news, we will present the performance and feasibility of the MDS as a powerful structural tool for very thin films.

References

1. J. Jaklevec, J.A. Kirby, M.P. Klein, A.S. Robertson, G.S. Brown, and P. Eisenberger: Solid State Commun. *23*, 679 (1977).
2. N.W. Cheung, R.J. Culbertson, L.C. Feldman, P.J. Silverman, and J.W. Mayer: Phys. Rev. Lett. *45*, 120 (1980).

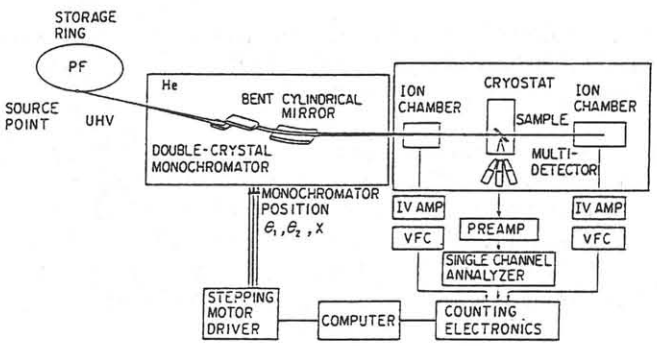

Fig. 1 Schematic diagram of the multi-detector fluorescence-detected x-ray absorption spectrometer.

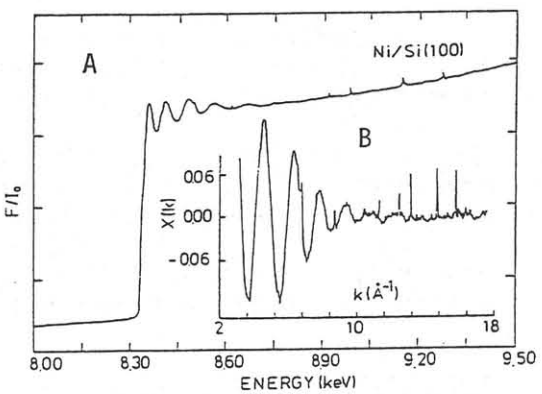

Fig. 2 Ni K-edge absorption spectrum of ion beam bombarded Ni/Si(100), (a), and extracted EXAFS oscillations, (b).