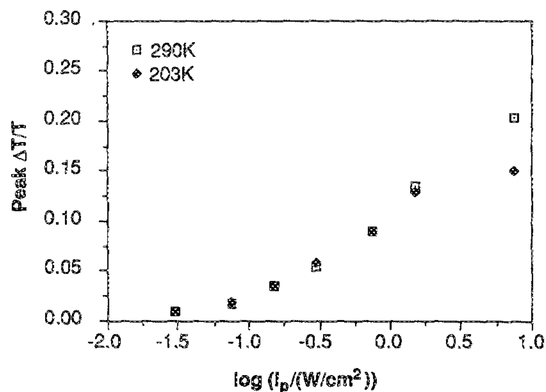

FIG. 4. Experimental pump power dependence of the peak transmission modulation (minimum near bulk band gap in the transmission spectra) on the pump intensity for sample No. 2 at two different temperatures.

to the Franz–Keldysh effect described previously for doping superlattices, also includes the effect of band-gap shrinkage due to the photoexcited charge carriers.

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Temperature-dependent transmission extended electron energy-loss fine-structure of aluminum

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Inelastic electron scattering experiments in a transmission electron microscope provide a probe of core electron excitations that have binding energies below 2 keV, and that are localized within submicron diameter sample volumes. Extended electron energy-loss fine-structure measurements which show the variation with temperature of the mean squared relative displacement of aluminum yield a localized measurement of the Debye temperature which is in excellent agreement with macroscopic measurements.

Transmission extended electron energy-loss fine-structure (EXELFS) data from submicron diameter regions of a thin aluminum foil have been obtained between 86 and 236 K. Analysis of the nearest-neighbor EXELFS signal in terms of the mean squared relative displacement (MSRD) has yielded a method for the estimate of the Debye temperature (Θ_D). The combination of a transmission electron microscope and a high collection efficiency electron energy-loss spectrometer provides Θ_D measurements localized within an extremely small volume element (approximately $10^{-2}\,\mu m^3$).[1] The data reduction procedures that were employed are identical to those applied to studies of temperature-dependent extended x-ray absorption fine structure (EXAFS).[2–6] Values of Θ_D can be related to microscopic inhomogeneities of fundamental properties such as elastic constants and heat capacity.[7]

Excellent signal-to-noise characteristics were made possible by the use of a parallel detection data acquisition system which has been discussed previously.[8] Improvements in detective quatum efficiency over serial acquisition system have made it possible to achieve the high statistical accuracy required for EXELFS studies at high (> 1 keV) energy losses where the inelastic scattering cross sections are extremely small.

Aluminum K edge spectra (Fig. 1) were obtained with a Philips EM430 electron microscope operated at 300 kV with a beam current of 5 nA into a 500-nm probe. The energy resolution at the detector was ~3 eV with a dispersion of

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1 eV per channel. Total acquisition times were 100 s for each 1024 channel spectrum. The coupling between the electron microscope and spectrometer was such that scattering was detected from a volume element with a diameter of 250 nm. The actual maximum number of electron counts per channel in the Fig. 1 spectrum was 2×10^7. Gain fluctuations of the system were removed from the spectra by division with a smoothed hole count spectrum. A liquid-nitrogen stage equipped with a heating element was used to control the temperture. Three Al K edges were acquired at each temperature in roughly 30-K steps between 86 and 236 K.

The sample thickness was estimated as a fraction of the total inelastic mean-free path according to $t/\lambda_T = -\ln(I_0/I_T)$, where I_0 is the elastic peak intensity and I_T the total current up to a maximum energy loss (1200 eV).[9] The sample volume analyzed showed a total inelastic mean-free-path fraction t/λ_T of 0.6 for the collection semiangle of ~ 100 mrad and 300-kV accelerating voltage. Multiple inelastic scattering is not expected to be significant for this sample thickness. The total mean free path λ_T can be estimated using values given by Egerton and Cheng for 100-kV incident electron (85 mn), and then scaling to allow for 300-kV electrons to obtain $\lambda_T \sim 180$ nm.[10,11] A value of t/λ_T of 0.6 thus corresponds to an approximate thickness of 110 nm. At this thickness, several nanometers of amorphous aluminum oxide scale are expected to cover each surface of the foil, and to contribute a significant signal to the depth-averaged transmission extended electron-energy-loss fine-structure spectroscopy (EXELFS).

The aluminum K absorption threshold was assigned to the position of the inflection point in the absorption edges. A cubic spline polynomial with five knots evenly spaced between 1565 and 2264 eV was fit to the high-energy side of the absorption edge and substracted to isolate the EXELFS oscillations. The EXELFS oscillations were normalized to the edge height calculated from the difference between a linear fit to the pre-edge region and the fit to the post-edge region. The $\chi(k)$ was weighted by the first power of k to amplify the high k part of the spectrum. The nearest-neighbor EXELFS oscillations can be described using the standard single-scattering formula[6]

$$\chi_1(k) = A_1(k)\,(N_1^2/R_1)\exp(-2k^2\Delta\sigma_1^2) \times \sin[2kR_1 + \delta_1(k)]. \quad (1)$$

In Eq. (1) $A_1(k)$ is the electron backscattering amplitude function characteristic of aluminum, N_1 is the number of atoms in the first coordination shell, and $\Delta\sigma_1^2$ is the difference between mean-square relative displacements in the aluminum foil at two different temperatures.

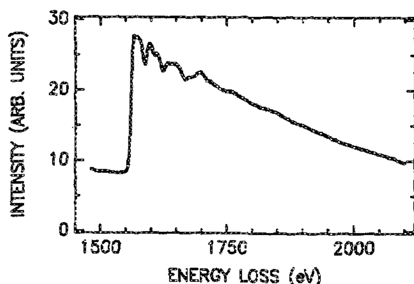

FIG. 1. Aluminum K edge obtained at 86 K.

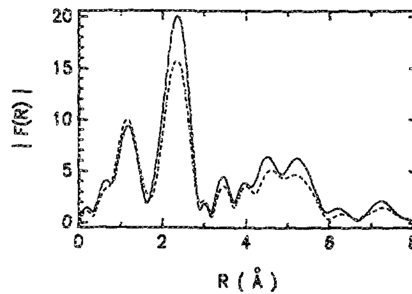

FIG. 2. Magnitude of Fourier transform of $k\chi(k)$ EXELFS for 86- and 236-K aluminum K edges.

Figure 2 shows the Fourier transforms (radial structure functions) of $k\chi(k)$ from samples at 86 K (solid line) and 236 K (broken line). Fourier transforms for this work were calculated with data between $k = 2.36$ and 10.05 Å^{-1}. The first peak in Fig. 2, which correspond to $R = 2.3$ Å, shows that the amplitude is due mainly to the first nearest neighbors. The actual distance is 2.871 Å, but no phase correction has been applied. The peak near 1.2 Å, which is clearly separated from the metal—metal bond length contribution, is probably due to the presence of surface oxide.

First nearest-neighbor oscillations $k\chi_1(k)$ were isolated with a 1.575–3.063-Å back-transform window on radial distribution functions in Fig. 2. Higher-temperature data were fitted by the 86-K data with the nearest-neighbor distance and coordination number held constant. Since the number and type of atoms is held fixed, such a fit yields the change in the experimental MSRD which is denoted by $\Delta\sigma_1^2$.

A fit of experimental $\Delta\sigma_1^2$ values with theoretical MSRD values relative to the lowest-temperature data was performed in order to estimate the Debye temperature. The temperature dependence of the nearest-neighbor MSRD based on the correlated Debye model of the density of states, $(\sigma_1^2)_D$, is given by

$$(\sigma_1^2)_D = 2\langle u^2\rangle(1-\gamma_1) = 2(\text{MSD} - \text{DCF}), \quad (2)$$

where the mean-squared displacement (MSD) and displacement correlation function (DCF) are defined in terms

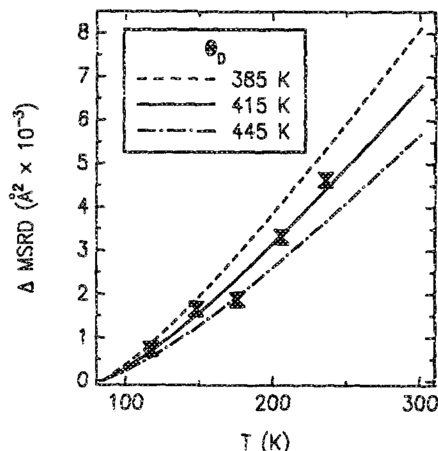

FIG. 3. Data (symbols) and theoretical Δ MSRD curves at the minimum deviation Debye temperature and ± 30 K.

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of the Debye function.[12,13] Equation (2) correctly shows that the MSRD is twice the difference between the MSD and DCF, which differs by a factor of 2 from Eq. (19) in the paper by Beni and Platzman. The minimum deviation between experiment and theory was found at $\Theta_D = 415$ K. This might be compared with literature values of Θ_D for bulk Al, e.g., 428 K (Ref. 14) and 396 K.[7] Figure 3 shows theoretical Δ MSRD curves for three values of Θ_D along with the experimental $\Delta\sigma_1^2$ values obtained with the lowest-temperature data as a reference. Agreement between the variation of the theoretical Δ MSRD and experiment is best for a Θ_D of 415 K. Calculated Δ MSRD curves for Θ_D values of 385 and 445 K show poor agreement with experiment.

High statistical quality transmission EXELFS data make quantitative studies of structural details from extremely small sample volumes possible. A parallel detection data acquisition system was necessary to achieve sufficient counting statistics in a short enough time to isolate the inelastic scattering from the microscopic region of interest. Excellent agreement was obtained between the transmission EXELFS determined Debye temperature and values given in the literature. This suggests that the temperature measurements were not significantly affected by the high flux of the incident electron beam. Future applications of this work might include the estimation of defect densities from values of $\Delta\ \sigma_1^2$ localized at interfaces or within minority phases.[15]

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Effects of deuterium plasmas on silicon near-surface properties

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The effects of reactive-ion etching and plasma etching (using deuterium) on the electrical properties of silicon have been studied employing capacitance-voltage measurements of Schottky diodes and secondary ion mass spectrometry. Both significant hydrogen penetration, which causes electrical deactivation of the boron dopant, and radiation damage result from the plasma exposure. A model is suggested to explain our results.

Reactive-ion etching is technologically important in the production of integrated circuits. For selective etching of silicon-dioxide over silicon, a CF_4/H_2 plasma is often used.[1] However, exposing a silicon surface to CF_4/H_2 is known to introduce hydrogen into the silicon crystal.[2,3] Hydrogen interacts with acceptors in silicon forming pairs, e.g., the boron-hydrogen pairs, which are electrically inactive.[4,5] More complex defects related to hydrogen have also been reported,[6,7] e.g., heavily damaged regions and {111} and {100} platelets. In reactive-ion etching (RIE) the silicon surface is exposed to bombardment of ions with energies typically in the range 200–500 eV causing subsurface damage,[7,8] while in plasma etching (PE) the energy of the bombarding ions is of the order of 30 eV, and the probability of atomic displace-

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