Interfacial Structure of Sc/Si Multilayers

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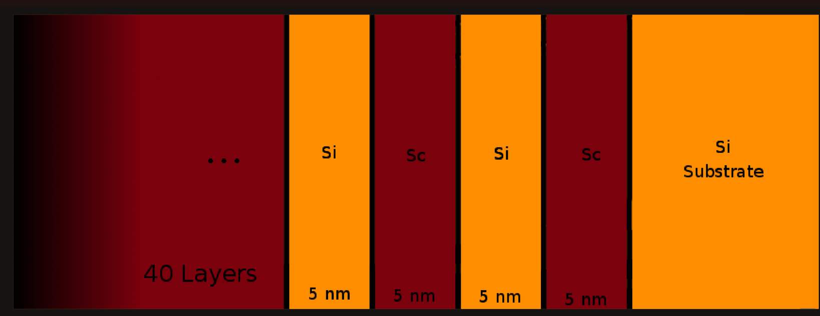
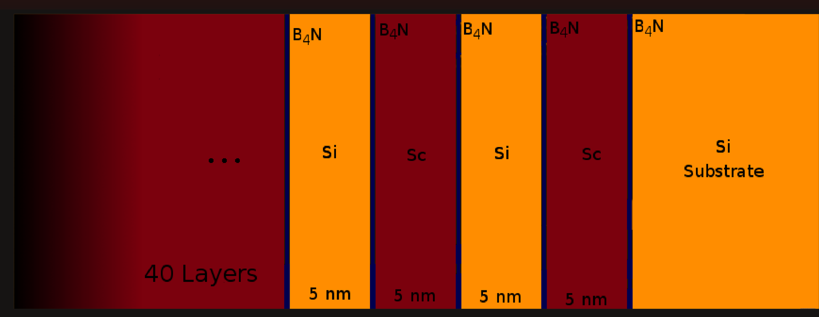
Abstract

Multilayers of scandium and silicon show promising reflectivity in the x-ray range of 35-50 nm. However, experimental samples fail to perform as predicted due to inter-diffusion of layers. We have investigated the intermixing of layers in $[Sc(5\ nm)/Si(4\ nm)]_{40}$/ Si multilayer reflective coatings prepared by periodic magnetron sputtering and annealed at 100, 200, 300, 400 and 500 ºC. Synchrotron excited scandium $L_{2,3}$ soft X-ray emission and absorption spectra of multilayers probe occupied Sc 3d4s-states. Using IRIS, we have studied the Si K_β x-ray emission spectra from silicon atoms within the multilayers and reference samples. The system is shown to be inevitably metastable and inter-diffusion of layers readily occurs. To determine the chemical nature of the layers upon degradation of the multilayer system, the multilayer spectra is compared to the spectra of reference samples (ScSi and Sc_5Si_3 silicides).

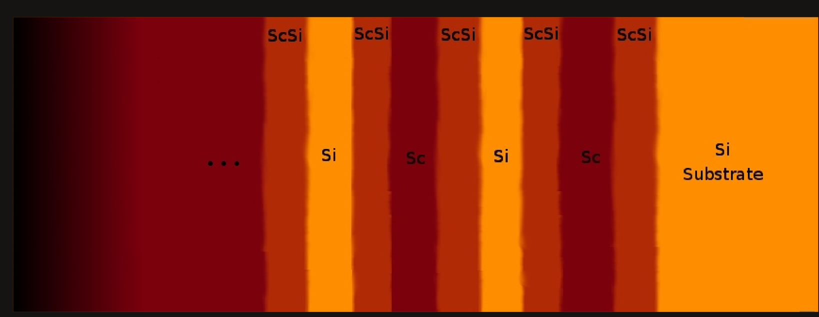
Thin barriers layers of boron carbide inserted between the Sc and Si layers reduce inter-diffusion. We have compared the local structure of Sc and Si atoms in Sc/Si multilayers and $[Sc(5\ nm)/B_4C(0.9\ nm)/Si(5\ nm)/B_4C(0.9\ nm)]_{40}$/ Si multilayers at a variety of annealing temperatures. The presence of B_4C barriers in $Sc/B_4C/Si/B_4C$ significantly delays the growth of intermixed regions. While scandium silicide is formed at an annealing temperature of 400 ºC in recently manufactured binary Sc/Si samples, it does not form at all in the temperature range investigated when the B_4C barrier layers are present. Likewise, the $Sc/B_4C/Si/B_4C$ samples maintain layers of distinctly separate species after extended shelf time while simple Sc/Si shows an increase in silicide content at lower annealing temperatures with sample aging.



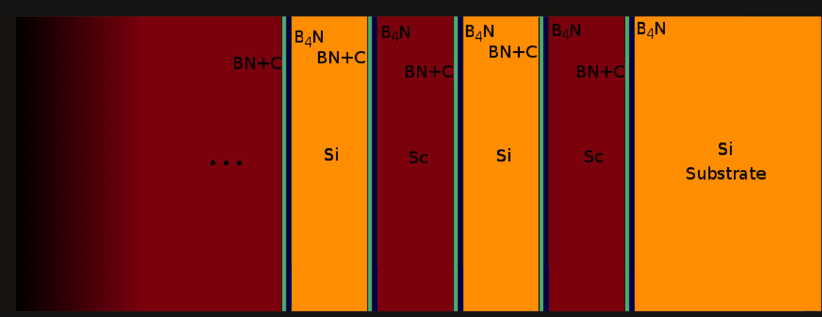
Schematic A.
Ideal Sc/Si multilayer on Si substrate.



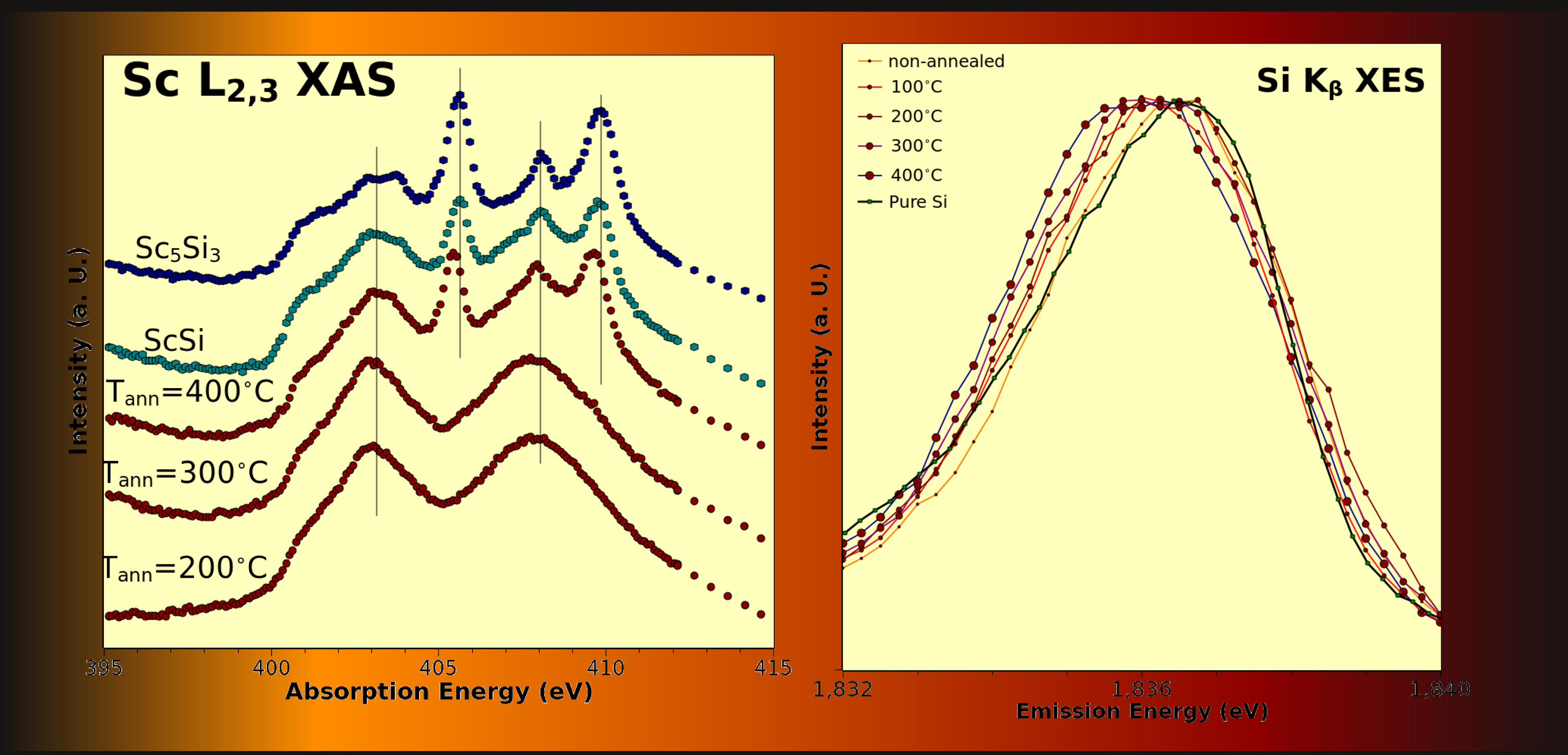
Schematic C.
To reduce intermixing of species, a B_4C barrier laminatant separates each layer.



Schematic B.
Actual Sc/Si multilayers have intermixed regions.
The inter-diffused silicide is shown below to be ScSi.



Schematic D.
It is shown that the barrier layers are contaminated with nitrogen during the annealing process.



Layer Inter-Diffusion

Theoretical predictions give values up to 72% reflectivity but experimental reflectivities of Sc/Si multilayers do not yet exceed 54% [1]. This is due to phase instability of the Sc-Si system, resulting in interaction and intermixing of layers both in as-deposited state and after production. The Si species tend to inter-diffuse into Sc layers [2].

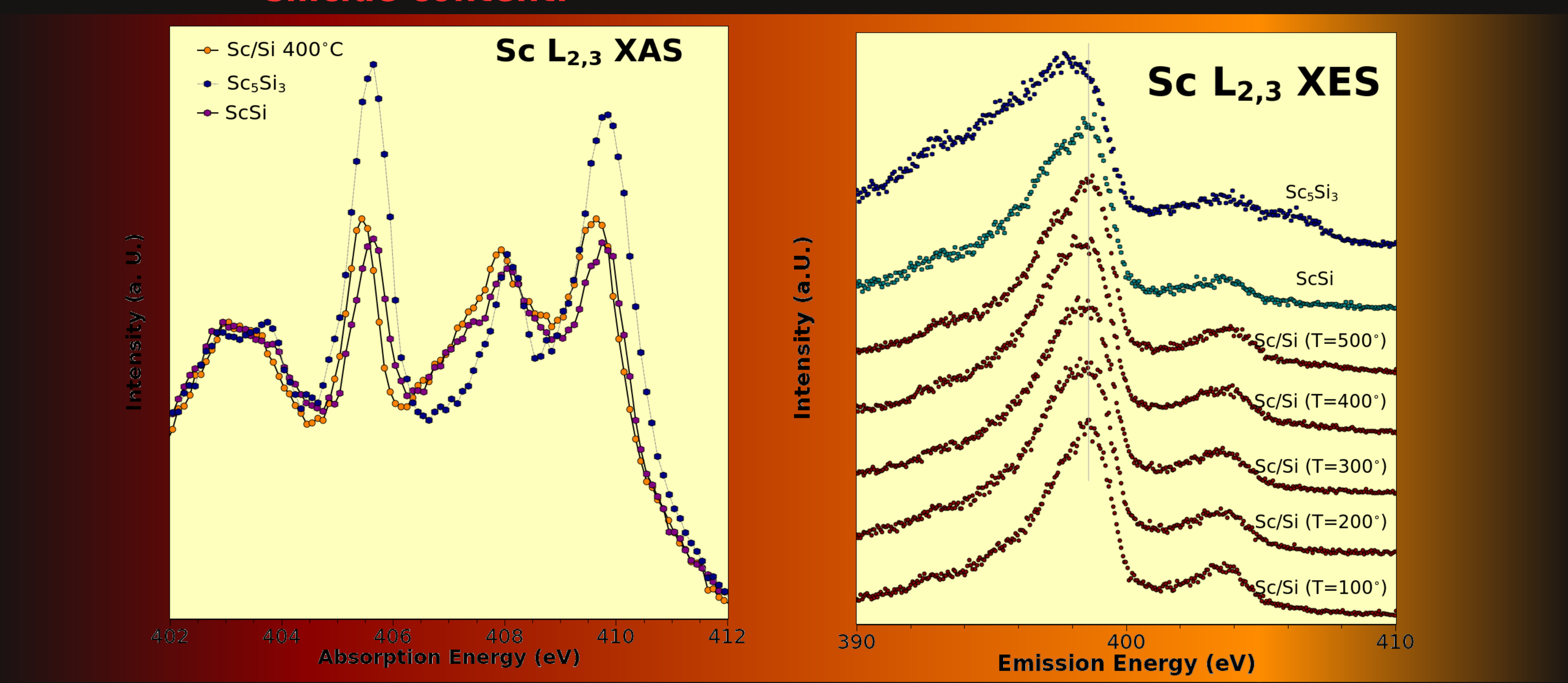
The absorption spectra (XAS) is shown to the far left. The spectra that characterizes distinctly separate layers is evident for Sc/Si annealed at temperatures of 200 and 300 ºC. At 400 ºC, the Sc/Si spectrum resembles that of the two scandium silicides, ScSi and Sc_5Si_3. Temperatures of 300 ºC are not enough to cause significant inter-diffusion; however, annealing at 400 ºC results in intermediary mixed layers.

The shape of the Si K_β emission spectrum (XES to the immediate left) evolves continuously away from pure Si with increasing annealing temperature in Figure 1b. This suggests that the silicide content within the multilayer increases with annealing temperature until at 400 ºC there is non-neglible silicide content.

Intermixed Silicide Identification

Silicide species is determined using the Sc $L_{2,3}$ XAS measurements. Species is suggested by the relative intensity and shape of the four features. The figure to the immediate right indicates that it is highly likely that the silicide species is not Sc_5Si_3 since the intensities of the 405.7 and 409.8 eV features are much greater. The spectrum of Sc/Si annealed at 400 ºC more closely resembles the ScSi reference spectrum.

Sc $L_{2,3}$ XES (shown at the far right) features do not distinguish between distinctly separate layers and intermixed ScSilayers. However, the emission spectra of Sc_5Si_3 exhibits a significant energy shift down to 396.9 eV. No shift is seen at any annealing temperature and so Figure 2b verifies the previous XAS conclusion.

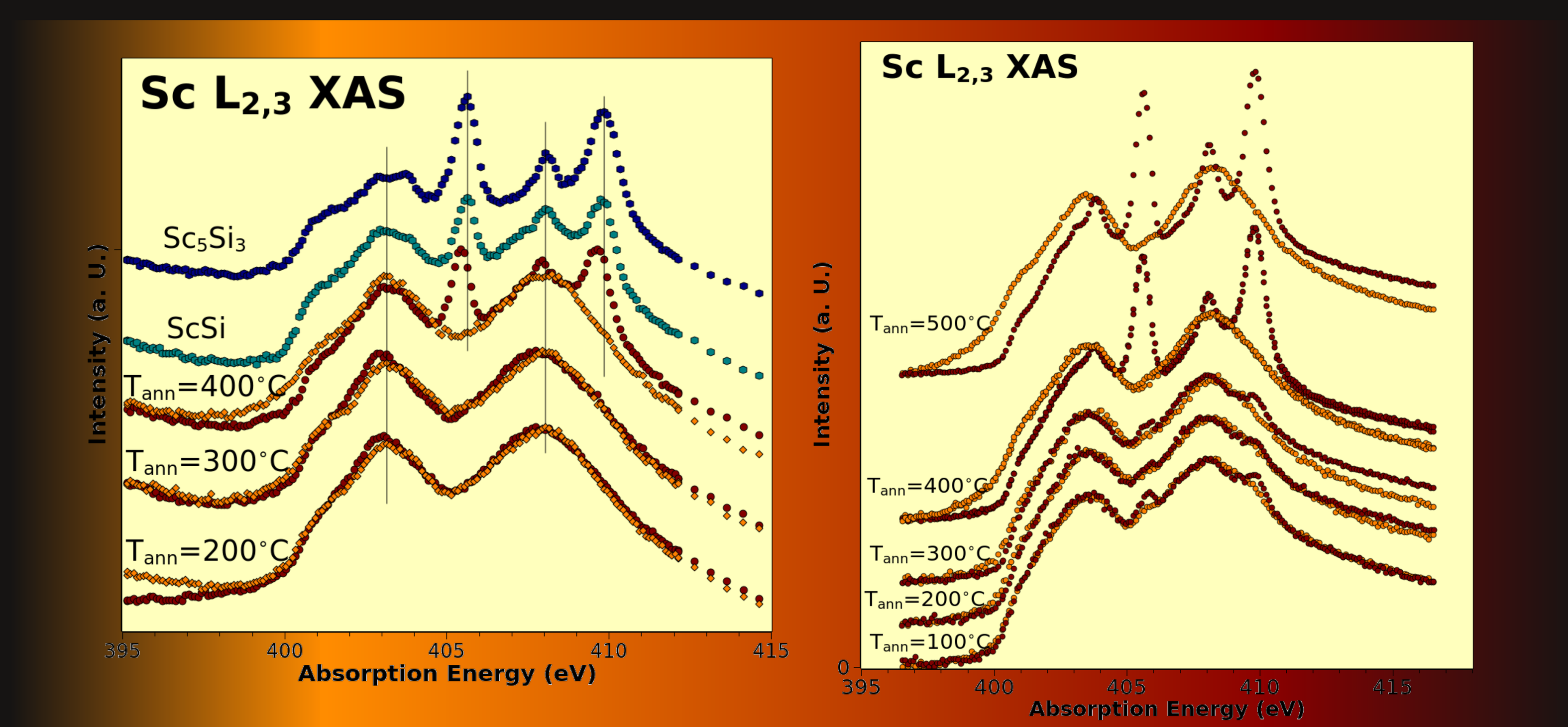


Barrier Layers

Thin barrier layers, such as W, Cr, ScN or B_4C [3, 4, 5, 6], inserted between the Sc and Si layers reduce inter-diffusion. The latter two are preferable because tungsten and chromium are highly absorbent.

The far left figure shows the XAS of Sc/Si and $Sc/B_4C/Si/B_4C$. At 400 ºC the Sc/Si has developed spectra highly resembling scandium silicides but the $Sc/B_4C/Si/B_4C$ maintains the spectral characteristics of distinct species.

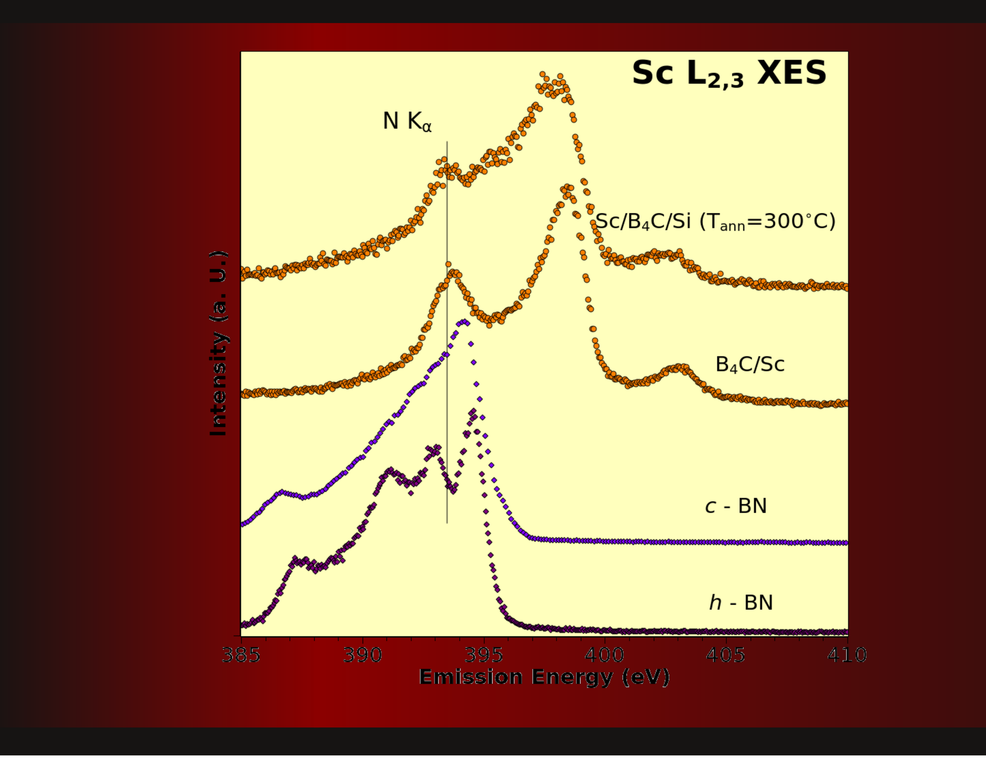
XAS measurements (immediate left) show that even after a three month shelf-life, samples containing B_4C barrier layers maintain distinct layers with no intermixing even at 500 ºC.



Barrier Structure

The XES spectra of multilayers containing the B_4C barrier layers differ from the Sc/Si spectra that was shown above. The XES to the right shows a low energy feature at 393.4 eV present for all annealing temperatures. This feature originates from neither the boron nor carbon. It is precisely where a nitrogen K_α emission band is expected.

Sintering boron carbides under inert atmospheres in the presence of nitrogen results in the formation of boron nitride [7] following the reaction $B_4C + 2N_2 = 4BN + C$. Nitrogen contamination does not exclude the use of boron carbide laminants as barriers as evidenced by the improvements seen above.



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