Soft X-ray Fluorescence Study of Buried Silicides in Antiferromagnetically Coupled Fe/Si Multilayers

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Abstract

Soft x-ray fluorescence spectroscopy has been employed to obtain information about the Si-derived valence band states of Fe/Si multilayers. The valence band spectra are quite different for films with and without antiferromagnetic interlayer exchange coupling, demonstrating that these multilayers have different silicide phases in their spacer layers. Comparison with previously published fluorescence data on bulk iron silicides shows that the Fe concentration in the silicide spacer layers is substantial. Near-edge x-ray absorption data on antiferromagnetically coupled multilayers in combination with the fluorescence data demonstrate unambiguously that the silicide spacer layer in these films is metallic. These results on the electronic structure of buried layers in a multilayer film exemplify the wide range of experiments made possible by new high-brightness synchrotron sources.

75.50.Bb,78.70.En,61.10.Ht,68.65.+g,71.20.Be

I. INTRODUCTION

Multilayer films made by alternate deposition of two materials play an important role in electronic and optical devices such as quantum-well lasers and x-ray mirrors.[1] In addition, novel phenomena like giant magnetoresistance and dimensional crossover in superconductors have emerged from studies of multilayers. While sophisticated x-ray techniques are widely used to study the morphology of multilayer films, progress in studying the electronic structure has been slower. The short mean-free path of low-energy electrons severely limits the usefulness of photoemission and related electron spectroscopies for multilayer studies.

Soft x-ray fluorescence (SXF) is a bulk-sensitive photon-in, photon-out method to study valence band electronic states.[2] Near-edge x-ray absorption fine-structure spectroscopy (NEXAFS) measured with partial photon yield can give complementary bulk-sensitive information about unoccupied states.[3] Both these methods are element-specific since the incident x-ray photons excite electrons from core levels. By combining NEXAFS and SXF measurements on buried layers in multilayers and comparing these spectra to data on appropriate reference compounds, it is possible to obtain a detailed picture of the electronic structure.

The Fe/Si multilayer system well illustrates the power of combining the SXF and NEXAFS techniques. Fe/Si multilayers exhibit a large antiferromagnetic (AF) interlayer exchange coupling that is apparently similar to that previously observed in metal/metal multilayers like Fe/Cr.[4] The observation of strong antiferromagnetic coupling was initially surprising, since this coupling is believed to be a manifestation of spin-density oscillations in the non-magnetic metallic spacer layer of a multilayer.[5] The interpretation of the Fe/Si coupling data was hampered by lack of knowledge about the strongly intermixed iron silicide spacer layer, which was variously hypothesized to be a metallic compound in the B2 CsCl structure[4] or a Kondo insulator in the more complex B20 structure.[6] If the spacer layer is not metallic, then the usual theories of interlayer exchange coupling do not apply[5] and the coupling must involve a novel mechanism. Using transmission electron microscopy (TEM), the spacer layer has been identified as a metastable cubic iron silicide closely lattice-matched to bulk Fe.[7] However, since the exact stoichiometry of the silicide was not determinable by diffraction means, the question of whether the spacer layer is a metal or not has remained unanswerable. SXF and NEXAFS are ideal techniques to resolve exactly this type of issue.

SXF and NEXAFS measurements were performed on five different Fe/Si multilayer films at the Advanced Light Source on beamline 8.0, which is described in detail elsewhere.[8] SXF data has previously been used to study buried layers of BN[9] and Si.[10] Data taken at the Fe L-edge closely resembles bulk Fe for all Fe/Si multilayers. NEXAFS spectra were acquired by measuring the total Si L-emission yield with the same detector used for fluorescence. The resulting data are expected to be comparable to those acquired by electron counting.[3] The films used in this study were grown using ion-beam sputtering (IBS) in a chamber with a base pressure of 2×10^{-8} torr. The deposition conditions were the same as those used in previous studies.[7] All multilayers were characterized using x-ray diffraction and magnetometry. Reference spectra were obtained from a crystalline silicon (c-Si) substrate piece, an amorphous silicon (a-Si) film made by IBS, and a fragment of an $FeSi_2$ sputter target.

II. RESULTS

Figure 1 shows hysteresis loops for three representative Fe/Si multilayers. The polycrystalline (Fe30Å/Si20Å)x50 multilayer grown on glass has a magnetization curve that shows no sign of interlayer exchange coupling. This multilayer has magnetic properties like those of bulk Fe. The epitaxial (Fe40Å/Si14Å)x40 multilayer grown on MgO has a low remanent magnetization and a high saturation field, which are the classic signs of antiferromagnetic interlayer coupling. Data on the polycrystalline (Fe30Å/Si14Å)x50 multilayer fall somewhere in-between these two extremes. Detailed characterization of these films has been published previously.[7]

For purposes of comparison to the Fe/Si multilayer SXF spectra, SXF reference spectra taken at the Si L-edge for the c-Si and a-Si samples are shown in Fig. 2. The spectra resemble previously published Si data.[2,10] The peaks near 89 and 92 eV in the c-Si spectrum originate from non-bonding s states and sp-hybridized states, respectively.[10,11] These features are broadened by disorder in a-Si.

Figure 3 shows the Si L-edge valence band emission spectra of the $FeSi_2$ reference sample and the same two polycrystalline Fe/Si multilayers whose magnetization data are shown in Figure 1. The $FeSi_2$ data has two primary features, namely s-orbital features near 90 eV, and a shoulder which extends up to 99 eV and is comprised mostly of states with d symmetry. These features have been previously identified in semiconducting bulk $FeSi_2$ specimens.[11]

In Fig. 3 the spectrum for the polycrystalline antiferromagnetically coupled multilayer with t_{Si} = 14Å looks similar to the $FeSi_2$ data, while the spectrum for the polycrystalline uncoupled multilayer with t_{Si} = 20Å is more like c-Si. Peaks in the AF-coupled multilayer spectrum are noticeably narrower than those in the $FeSi_2$ reference spectrum. Studies of bulk iron silicides have shown that peaks in the Si emission spectra narrow as the iron content increases and Si-Si coordination decreases.[11] Thus the data of Fig. 3 indicate that the Fe atomic fraction in the spacer layer of the AF-coupled multilayers is higher than 1/3. Overall the shape of the spectrum from the AF-coupled multilayer is more reminiscent of SXF data on bulk B20 FeSi than of data on bulk $FeSi_2$.[11] The uncoupled multilayer data in Fig. 3 have a sharp peak near 92 eV which coincides with a feature in the c-Si spectrum although the shape of the higher energy part of the valence band more closely resembles the $FeSi_2$ data. The narrowness of the 92 eV feature is evidence for a significant Fe content and low Si-Si coordination in the spacer layer of the uncoupled multilayer. These observations are consistent with the TEM determination that the spacer layer in the uncoupled multilayers is amorphous iron silicide.[7]

The presence of significant Fe in the silicide spacer layer of the Fe/Si multilayers strongly suggests that the silicide is metallic. Unambiguous confirmation of the metallic nature of the silicide is obtained by plotting together the SXF and NEXAFS spectra as in Fig. 4. For this data set the spectrometer energy calibration was accomplished through comparison with earlier work on c-Si L-emission[12] and through alignment of the elastically scattered photon peak to the incident photon energy. The overlap of the valence band features from the SXF and the conduction band features from NEXAFS is therefore convincing evidence that the silicide spacer layer of the multilayer is metallic. While the Si bands near the Fermi level clearly show the energy gap which is expected in a semiconductor, the slope of the silicide bands near E_F suggests that the Fermi level falls in the middle of an energy band. A more detailed interpretation of these spectral features will require electronic structure calculations.

III. DISCUSSION AND CONCLUSIONS

SXF data have also been taken on an Fe/Si multilayer with t_{Si} = 14Å but which was held at a reduced temperature of 120 K during growth (data not shown). The valence band spectra of the film grown at reduced temperature with t_{Si} = 14Å look virtually identical to data on the film grown at 60°C but with t_{Si} = 20Å. The most likely explanation for this similarity is that both films have amorphous iron silicide spacer layers. The amorphous state of the spacer layer in these films must be due to the reduced Fe content compared with films which have thinner Si layers or are deposited at higher temperature. Multilayers with amorphous spacer layers do not display antiferromagnetic interlayer coupling.[4,7]

A comparison of the data of Figs. 3 and 4 show that the peaks in the spectrum of the epitaxial AF-coupled multilayer are narrower than those in the spectrum of the polycrystalline AF-coupled multilayer. This suggests that a higher degree of local order occurs in epitaxial films. The nature of this order and the exact structure of the silicide spacer layer phase are not yet known. TEM studies have shown that the spacer layer in AF-coupled multilayers is a crystalline cubic iron silicide in the B2 CsCl phase or fcc DO_3 phase.[7] The TEM diffraction patterns are not consistent with the B20 structure, whose SXF data most closely resembles that of the AF-coupled multilayers. Jia *et al.* do report SXF data on the DO_3-structure Fe_3Si phase but the spectrum of this compound has a much more prominent and narrow non-bonding s feature.[11] The presence of an Fe_3Si spacer can be ruled out on other grounds since this compound is ferromagnetic, inconsistent with the presence of antiferromagnetic interlayer coupling. The possibility remains, however, that the spacer layer is in the DO_3 structure but at a different stoichiometry. No SXF data on the metastable B2 silicide phase have been reported although photoemission measurements show that it is metallic.[13] The magnetic properties of the B2 phase and hypothetical off-stoichiometry phases are not known. The observation of large biquadratic coupling in Fe/Si multilayers[14,15] suggests that an antiferromagnetic or ferrimagnetic order may be present in the spacer layer.

When examined together, the SXF and NEXAFS data show that Fe/Si multilayers with crystalline metallic silicide spacer layers have antiferromagnetic interlayer coupling, while similar multilayers with amorphous silicide spacer layers show no interlayer coupling. Whether the amorphous silicide layers are metallic or semiconducting is a topic for further study. Theoretical calculations will be necessary to get a better estimate of the stoichiometry and magnetic properties of the silicide spacer in the AF-coupled multilayers. The present data should lay to rest any speculation that the interlayer exchange coupling in Fe/Si multilayers involves a novel mechanism. The clarity of these results on thin buried silicide layers illustrates the power of photon-counting spectroscopies with their intrinsic bulk sensitivity for the study of multilayer films.

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FIGURES

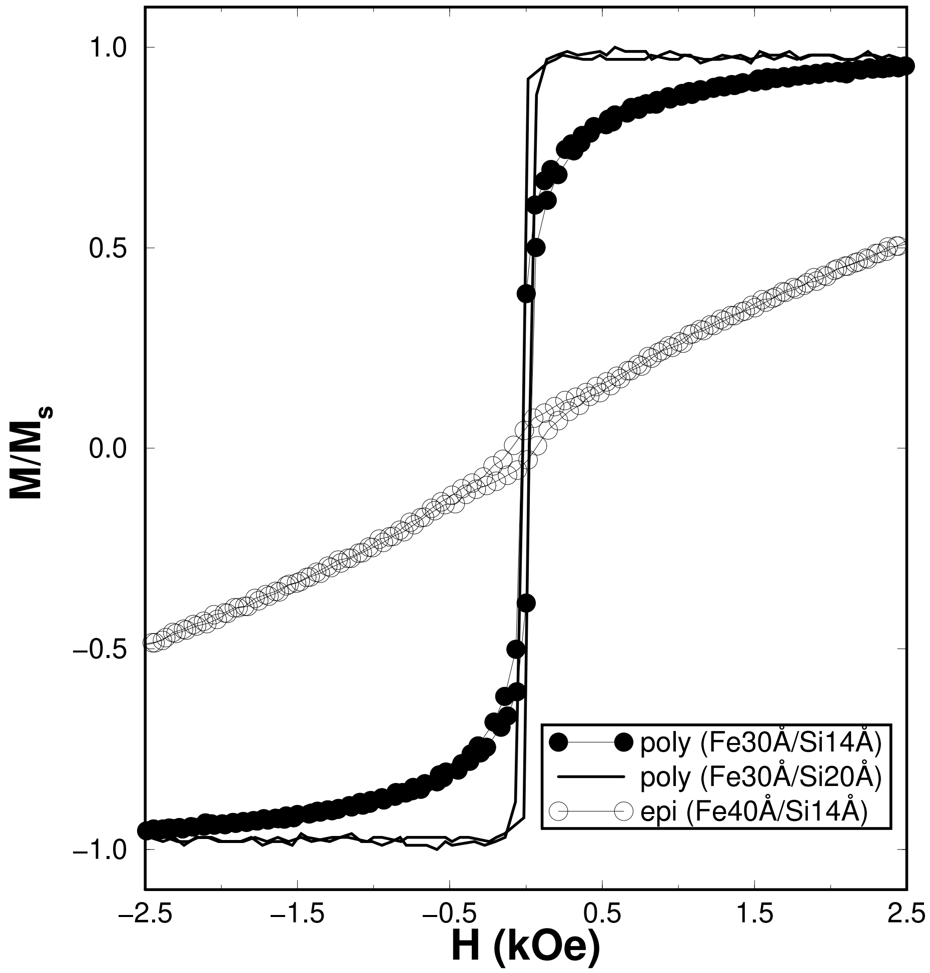

FIG. 1. Magnetization curves for three Fe/Si multilayers. The y-axis shows magnetization data normalized to the saturated value. The solid line indicates data for a polycrystalline (Fe30Å/Si20Å)x50 multilayer which has a magnetization curve much like bulk Fe. The open circles indicate data for an epitaxial (Fe40Å/Si14Å)x40 multilayer which has the high saturation field and low remanent magnetization that are characteristic of antiferromagnetic interlayer exchange coupling. The polycrystalline (Fe30Å/Si14Å)x50 multilayer (indicated by filled circles) has weaker antiferromagnetic coupling than the epitaxial multilayer.

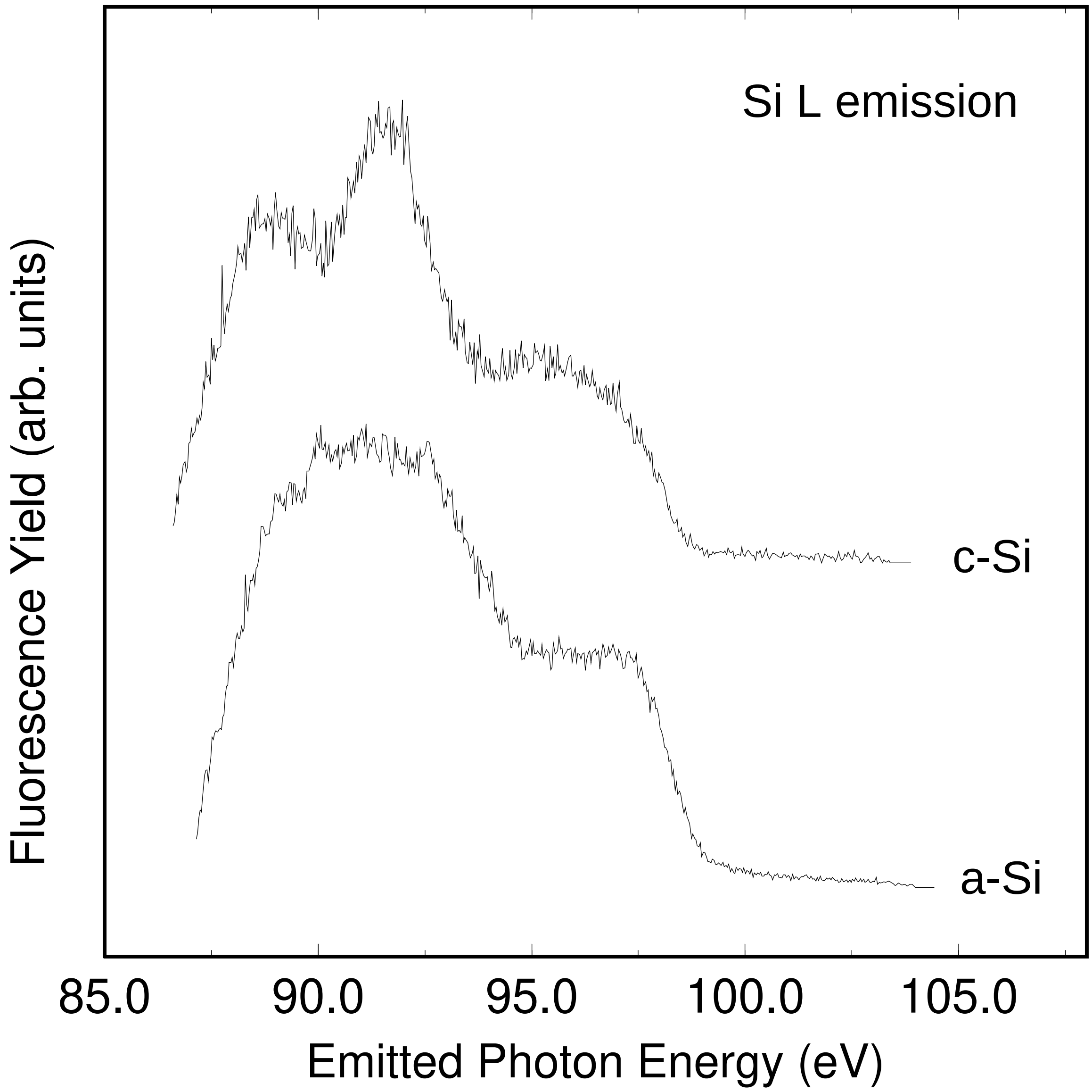

FIG. 2. SXF Si L-emission spectra for crystalline and amorphous silicon films. These data were taken with an incident photon energy of 132 eV.

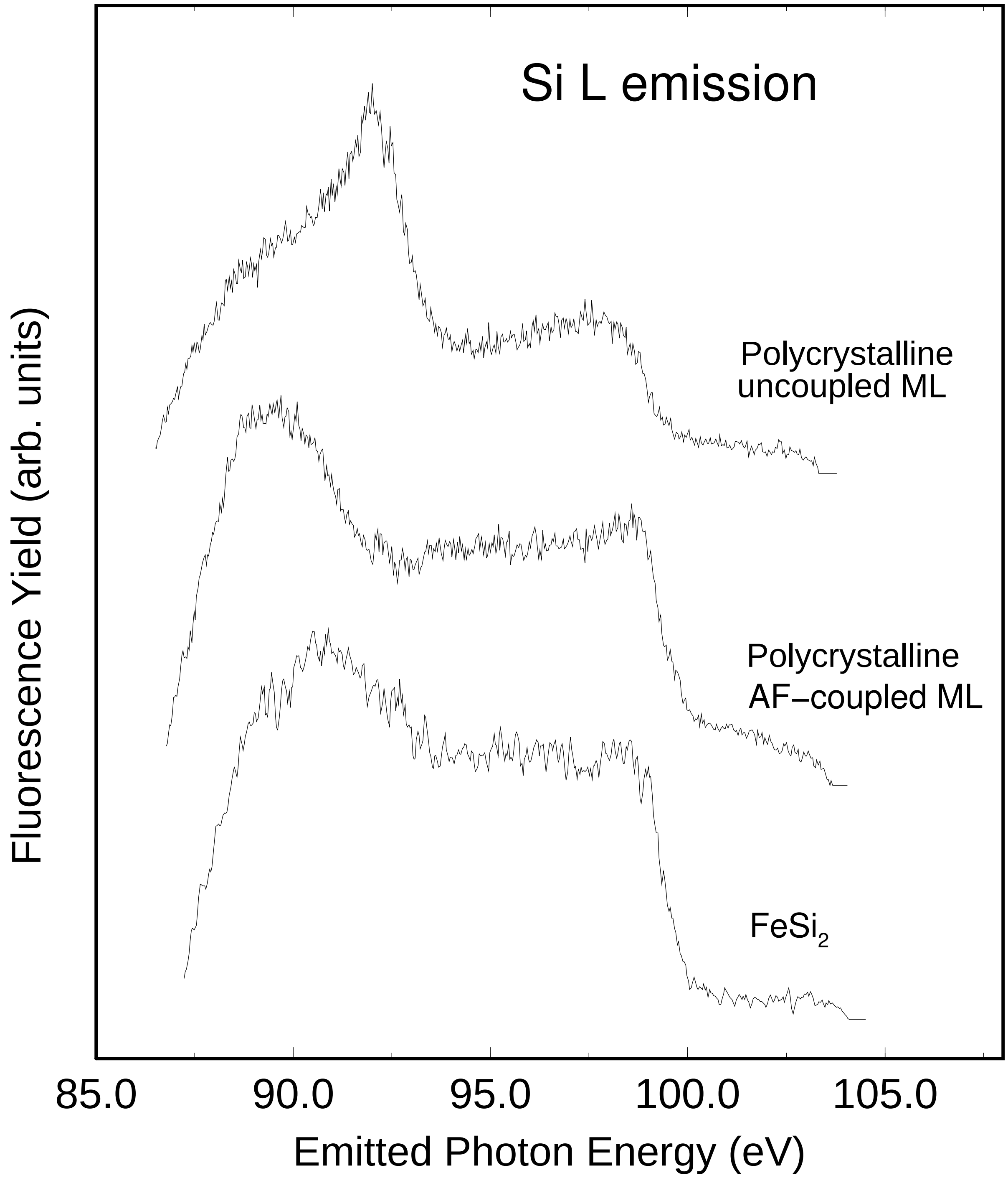

FIG. 3. SXF Si L-emission spectra for an $FeSi_2$ reference sample and for the two polycrystalline Fe/Si multilayers whose magnetization curves are shown in Figure 1. The incident photon energy was 132 eV. The data labelled "Uncoupled ML" is from the (Fe30Å/Si20Å)x50 multilayer grown on glass. The data labelled "AF-coupled ML" is from the antiferromagnetically coupled (Fe30Å/Si14Å)x50 multilayer grown on glass.

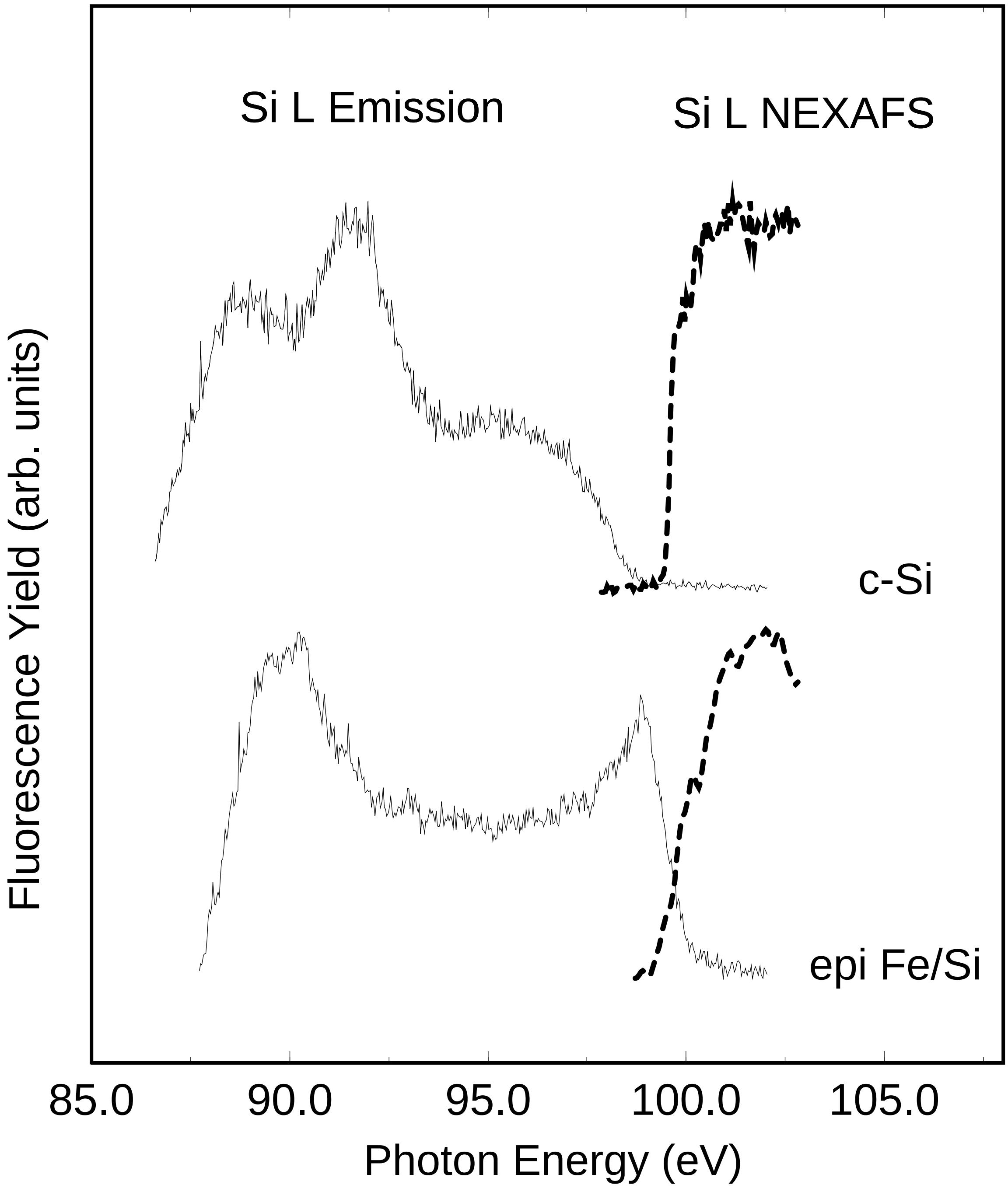

FIG. 4. SXF Si L-emission spectra (solid line) and Si L-edge NEXAFS (dashed line) for the crystalline Si reference film and for the epitaxial (Fe40Å/Si14Å)x40 multilayer on MgO. The crossing of the valence band data obtained from SXF and the conduction band data obtained from NEXAFS demonstrates that the silicide spacer layer is metallic.