Complex intermetallic phase in multicrystalline silicon doped with transition metals

Matthias Heuer,[1] Tonio Buonassisi,[1] Matthew A. Marcus,[2] Andrei A. Istratov,[1] Matthew D. Pickett,[1] Tomohiro Shibata,[3] and Eicke R. Weber[1]

[1]*Department of Materials Science and Engineering, University of California, Berkeley and Materials Science Division,
Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[2]*Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

[3]*Department of Physics, Illinois Institute of Technology, Chicago, Illinois 60616, USA*

We report the observation of an alloy phase with fluorite-type structure containing Ni, Fe, Cu, and Si, found as precipitates in multicrystalline silicon. The analysis of extended x-ray absorption fine-structure microspectroscopy (μ-EXAFS) measurements on the K edges of the transition metals of the precipitates and a synthetic reference material with composition of $Ni_{0.82}Fe_{0.21}Cu_{0.02}Si_{1.94}$ support a structure model similar to $NiSi_2$ but with mixed occupancies of Fe on the Ni site and Cu on the Si site. This observation provides evidence that transition metals interact during precipitation within silicon and form complex silicides.

Transition metals in silicon, such as iron, copper, and nickel, are the most detrimental unintentional contaminants in silicon, which can deteriorate silicon device performances in concentrations as low as $10^{10}–10^{11}$ cm^{-3}. The significance of transition metals for silicon materials science and technology has motivated extensive studies which resulted in thousands of publications in the last 40−50 years (see Refs. 1–3 for a review). The point of view generally accepted by the scientific community is that transition metals can be found in silicon as either interstitial or substitutional species, point defect complexes (e.g., interstitial-substitutional pairs), or single-metal silicide precipitates, such as Cu_3Si or $NiSi_2$. There are very few reports in which interactions between different metal species were studied.[4] In lieu of accurate data, it was often assumed that when several metals are present in the sample, these metals do not interact with each other, although they may co-precipitate at the same location.

The development of highly sensitive synchrotron based x-ray microscopy techniques made it possible to detect metal precipitates in silicon as small as 18 nm in radius and *in situ* determine their elemental composition and chemical state.[5,6] The application of these techniques to metal-contaminated multicrystalline silicon (mc-Si) samples enabled us to obtain evidence of a chemical interaction between Fe, Cu, and Ni with the formation of an intermetallic phase. Analysis of x-ray absorption spectra of this phase by means of computer modeling enabled us to determine its crystal structure.

Besides the fundamental physical value of observing a Ni, Fe, and Cu bearing phase in silicon, it has significant implications for the engineering of metal-related defects in silicon and their gettering and passivation. This problem is particularly important in silicon photovoltaics, where metals are considered the major culprit for losses in solar cell efficiencies.[7,8] The concept of metal nanodefect engineering, recently suggested by our group,[9] is based on a reduction in the detrimental impact of metals in solar cells by changing their spatial distribution or chemical state to achieve the lowest possible recombination activity of metal clusters. Clearly, it is instrumental to understand the properties and the mechanisms of formation of mixed silicides because, depending on their recombination properties, they may either be undesired species for which formation should be suppressed, or efficient internal gettering sinks for transition metals. Likewise, the gettering and hydrogen passivation of transition metal clusters depend on their chemical state, and may be different for intermetallic silicides than for single-metal silicides.

The phase discussed in this study has been observed in our studies of a variety of silicon materials, including multicrystalline float zone (mc-FZ) silicon, Czochralski grown silicon, and in as-grown commercial mc-Si from cast processes. The data presented in this article were obtained on a mc-FZ silicon[10] sample, which was contaminated with Ni, Fe, and Cu by scratching with a wire of the respective element and then annealed at 1200 °C for 2.5 h, leading to contamination levels of 1×10^{16} cm^{-3} for iron, 1×10^{18} cm^{-3} for copper, and 7×10^{17} cm^{-3} for nickel according the maximum solubility of these elements at the given temperature.[11] mc-FZ silicon was chosen because it contains a high density of grain boundaries and provides a high concentration of nucleation sites for metal precipitates. The sample was "slow cooled" from 1200 °C in the furnace over 12 h. The cooling rate was 25−30 K/min in the beginning of the cool, dropping down to 3−8 K/min in the medium temperature range (800−400 °C), and to even lower cooling rates by the end of the cool. Remaining silicides at the sample surface were removed by polishing and chemical cleaning.

To determine the precise location and speciation of metal-rich precipitates inside the mc-FZ sample, synchrotron-based micro-x-ray fluorescence (μ-XRF) and extended x-ray absorption fine-structure microspectroscopy (μ-EXAFS) were performed at beamline 10.3.2 (Ref. 12) of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. The focusing optics of 10.3.2 were adjusted to achieve x-ray spot sizes from (5×7) to (7×7) μm^2, at a peak flux of $\sim 3 \times 10^8$ photons/s. This beamline has a Si(111) monochromator with an energy resolution of ~ 1 eV. The ability of μ-XRF to detect metal-rich micro- and nanoclusters in silicon has been well established.[8,13,14] Further details of the ALS beamline 10.3.2 can be found in Refs. 15 and 12. Ni and Fe K edge EXAFS were measured at the Materials Re-
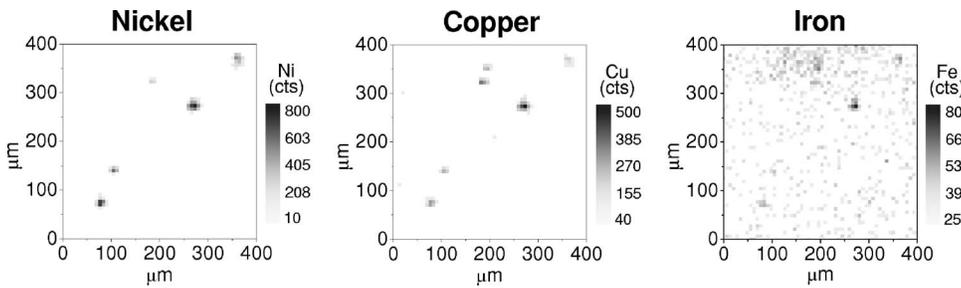
FIG. 1. XRF microscopy maps of mc-FZ silicon showing precipitates simultaneously containing Ni, Fe, and Cu as dark spots.

search Collaborative Access Team undulator beamline at the Advanced Photon Source, Argonne National Laboratory. A cryogenic double-crystal Si (111) monochromator was utilized for x-ray energy selection and an Rh-coated mirror was used for harmonic rejection. The incident photon intensity was measured by an ion chamber filled with a N_2 and He mixture. For the Fe K edge EXAFS, XRF intensity was measured by a conventional three-grid Stern-Heald-type ionization chamber detector filled with Ar gas. The absence of fluorescence correction was ensured by comparison with transmission EXAFS.

Ni K edge EXAFS were measured by transmission mode. For all scans, simultaneous measurement of reference foils eliminated the possibilities of energy shifts in the series of scans.

In addition to precipitates containing only one or two metal species, μ-XRF maps of many different slow-cooled mc-Si samples, as well as the mc-FZ material, frequently revealed metal-rich precipitates simultaneously containing Ni, Fe, and Cu (Fig. 1). μ-XRF analyses on several multim-etal precipitates consistently yielded a Ni:Fe:Cu ratio of approximately $10:\sim 1:3$ with an uncertainty of about $3-5\%$. To study the chemical nature of these clusters, μ-EXAFS measurements were performed at the K edges of Ni, Fe, and Cu. Because each compound has a unique EXAFS spectrum, a good correlation between μ-EXAFS spectra from the precipitates in silicon and reference materials, which are well characterized in structure and composition, yields a positive identification of chemical state.

To ascertain which phases could have formed, a Ni–Fe–Cu silicide sample was synthesized using an initial stoichiometry following the overall Ni:Fe:Cu ratio from μ-XRF measurements on the precipitates, and a transition metal to silicon ratio of 1:2, which corresponds to the most Si-rich phase of the metal-Si system (i.e., MSi_2). According to this
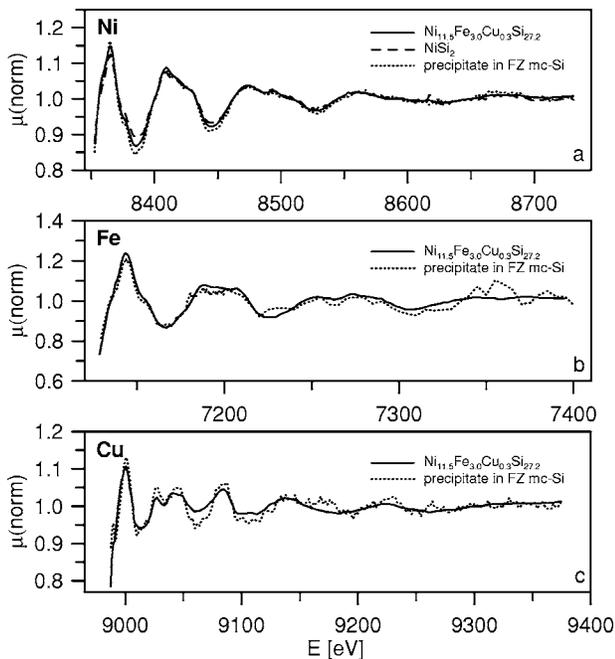

FIG. 2. EXAFS spectra of each transition-metal edge of precipitates in mc-FZ silicon and the synthetic reference material, $Ni_{0.82}Fe_{0.21}Cu_{0.02}Si_{1.94}$. Good match between all EXAFS spectra indicates the same atomic site occupancies in both phases. The Ni EXAFS (a) matches as well with pure $NiSi_2$, which supports that the investigated phases have a CaF_2-type $NiSi_2$ structure.
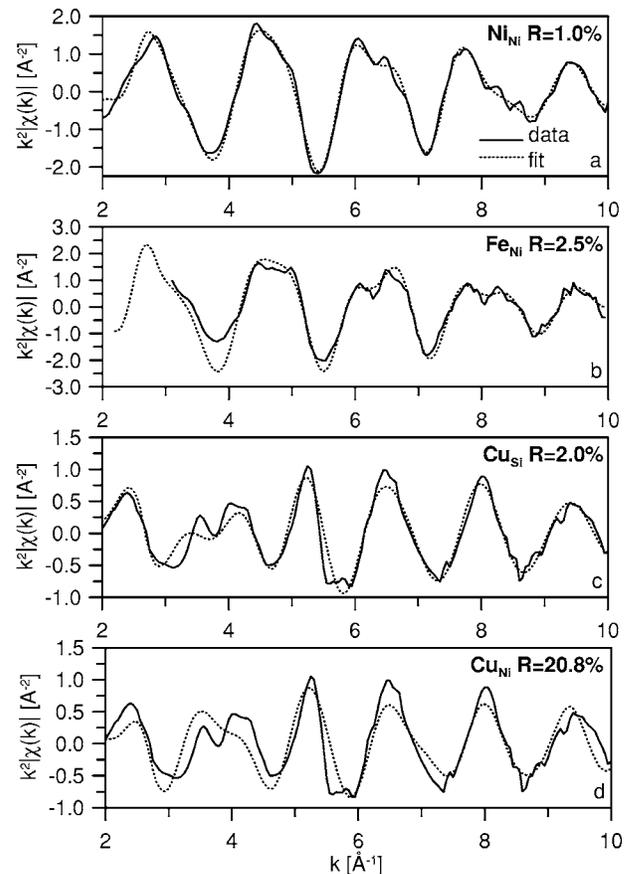

FIG. 3. EXAFS data and fits for each transition-metal edge: (a) Ni on the nickel site in $NiSi_2$, (b) Fe on the nickel site in $NiSi_2$, (c) Cu on the silicon site in $NiSi_2$, and (d) Cu on the nickel site in $NiSi_2$.
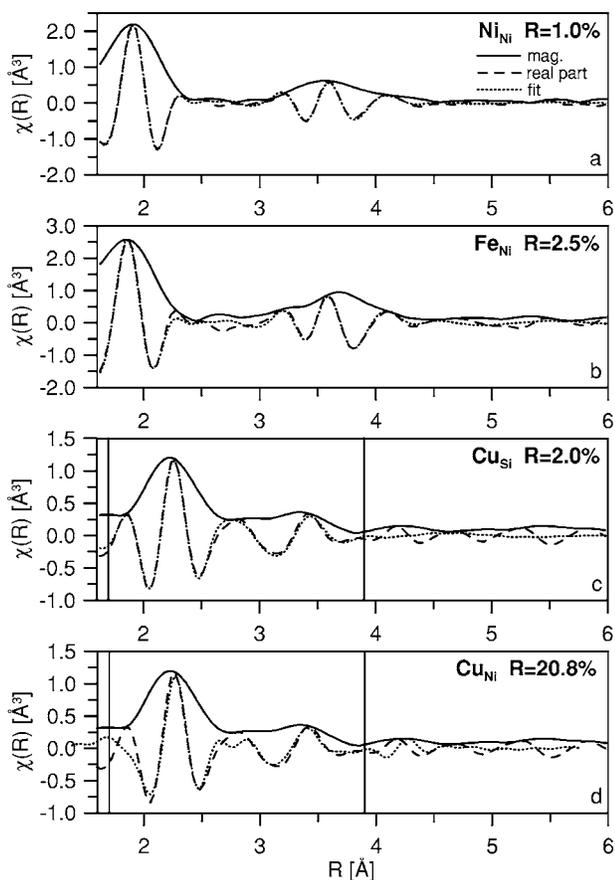
FIG. 4. Magnitude, mag., and real part, of Fourier transform of EXAFS data and fits for each transition-metal edge: (a) Ni on the nickel site in $NiSi_2$, (b) Fe on the nickel site in $NiSi_2$, (c) Cu on the silicon site in $NiSi_2$, and (d) Cu on the nickel site in $NiSi_2$. Note that the fitting range in (c) and (d) is between the vertical lines.

initial ratio, high-purity powders (99.999%) of the elements silicon, iron, nickel, and copper were mixed and homogenized by melting in a SiO_2 crucible at 1600 °C. The resulting melting ball was placed in an evacuated silica ampoule and annealed at $T = 1000$ °C for 7 days and then quenched in water.

The synthesis product was checked by an x-ray diffraction (XRD) measurement on a Seifert XRD3000 diffractometer (30 mA/40 kV; Bragg-Brentano geometry) equipped with a graphite (002) diffracted-beam monochromator and a scintillation detector. The powder-diffraction pattern, recorded from 5° to 100° 2θ with a step size of 0.05° 2θ and 2 s/step, confirmed that the resulting material was a mixture of silicon; two phases structurally similar to $NiSi_2$ (referring to the Joint Committee for Powder Diffraction Studies, JCPDS, standard number 43-0989) and smaller amounts of another phase similar to $Cu_3Ni_{10}Si_7$ (JCPDS 03-1061).

The chemical composition of the reference sample was then determined by electron microprobe analysis using a CAMECA SX100 operating at 15 kV/20 nA and using calibration standards of synthetic NiO, $CuFeS_2$, and $CaMgSi_2O_6$. It was found that the composition of the main phase in the reference sample is $Ni_{0.83(1)}Fe_{0.20(1)}Cu_{0.03(1)}Si_{1.97(1)}$. The secondary phases,

TABLE I. Refined EXAFS parameters and corresponding paths for copper on silicon site in $NiSi_2$, $R = 2.0\%$.

Parameters		Path
E_0	7.0 (1.2)	Used for all paths
S_0^2	0.763 (88)	Used for all paths
δR_1	0.138 (21)	$Cu_0 - Ni_{1\_1} - Cu_0$
δR_2	-0.094 (30)	$Cu_0 - Si_{2\_2} - Cu_0$
δR_3	$(\delta R_1 + \delta R_2)/2$	$Cu_0 - Si_{2\_2} - Ni_{1\_1} - Cu_0$
δR_4	0.047 (31)	$Cu_0 - Si_{2\_3} - Cu_0$
σ_1^2	0.007 (2)	$Cu_0 - Ni_{1\_1} - Cu_0$
σ_2^2	0.026 (6)	$Cu_0 - Si_{2\_2} - Cu_0$
σ_3^2	σ_2^2	$Cu_0 - Si_{2\_2} - Ni_{1\_1} - Cu_0$
σ_4^2	0.021 (5)	$Cu_0 - Si_{2\_3} - Cu_0$

$Ni_{1.01(1)}Cu_{0.13(1)}Si_{1.84(1)}$ and $Cu_{0.39(1)}Ni_{0.24(1)}Si_{0.36(1)}$, did not contain iron and were therefore not of interest for a phase identification of the mc-FZ precipitates.

To obtain a homogeneous reference material in a second synthesis, a powder mix was produced with an initial weight according to $Ni_{0.83}Fe_{0.20}Cu_{0.03}Si_{1.97}$, pressed to a pellet, and annealed in an evacuated silica ampoule at 900 °C for 2 days. The product was homogenized by grinding in an agate mortar, pressed again, and annealed a second time under the same conditions. The XRD measurement on the resulting material confirmed a single phase similar to $NiSi_2$ (JCPDS 43-0989) with a composition of $Ni_{0.82(1)}Fe_{0.21(1)}Ci_{0.02(1)}Si_{0.94(1)}$ which was determined by electron microprobe analysis.

The comparison of the Ni EXAFS spectra of: (a) The precipitates in the slow-cooled mc-FZ silicon, (b) pure $NiSi_2$, and (c) the synthesized reference material confirmed that all of these compounds have nickel in the same coordination as the CaF_2-type $NiSi_2$ structure [Fig. 2(a)]. The very good match between the EXAFS spectra of the mc-FZ precipitates and the standard exists for every measured element, indicating the same atomic site occupancies in both phases [Figs. 2(a)–2(c)]. Thus, it is obvious that their individual structures just differ in elemental substitutions on the atomic sites of the same structure type.

Further, the measured compositions $Ni_{0.83}Fe_{0.20}Cu_{0.03}Si_{1.97}$, $Ni_{1.01}Cu_{0.13}Si_{1.84}$ and $Ni_{0.82}Fe_{0.21}Cu_{0.02}Si_{1.94}$ imply that Ni and Fe share one site of the structure; and Cu and Si, the other site, since the summation of the formula units gives: $2[Ni,Fe]=[Si,Cu]$.

It was possible to confirm this assumption by analyzing the EXAFS data measured for Ni, Fe, and Cu at the precipitates, as well as for the reference material. Note that the oscillations in the Ni and Fe spectra are very similar, which suggests that both elements are in a similar structural environment, i.e., sharing the same site of the structure. In contrast, the oscillations in the Cu spectrum appear very different from the Ni and Fe spectra, implying that Cu has a different structural environment and occupies a different structural site.

Following these considerations, a structure model was developed to analyze the EXAFS data of the reference

material. This model is a derivative of the fluorite-type structure of $NiSi_2$ (space group $Fm\bar{3}m$), whereby 20% iron and 80% nickel share the Ni site ($4a$) and 99% silicon and 1% copper share the Si site ($8c$). The cubic lattice parameter $a=5.3957(2)$ Å was determined from the XRD of the reference material using silicon as the internal standard to correct the Bragg angles.

It is a well established procedure to analyze EXAFS data by modifying an *ab initio* calculated theoretical standard.[16] Hereby, a sum over multiple scattering calculations is used to predict an EXAFS signal from a structure model, and the differences between the calculated and the measured EXAFS signal are minimized using least-squares algorithms to find the best-fit set of parameters for the calculated signal. Based on the above-mentioned structure model, individual theoretical standards for each elemental EXAFS spectrum (Ni, Fe, Cu) were calculated using the computer program FEFF8.[17] Since the proposed structure contains mixed occupancies, which cannot be simulated directly with FEFF8, the final scattering contributions were calculated by a weighted averaging of different boundary situations. For example, the scattering path data for the Cu spectrum were generated by averaging FEFF8 culations for Cu on a Si site in pure $NiSi_2$, Cu on a Si site in a hypothetical "$FeSi_2$" structure, and Cu on a Cu site in hypothetical "$NiCu_2$" structure (both identical to $NiSi_2$). Hereby, the weighting scheme referred to the measured composition of $Ni_{0.82}Fe_{0.21}Cu_{0.02}Si_{1.94}$.

The refinements were performed with the program IFEFFIT[18] using 8–10 free parameters, including changes in the half-path lengths, δR_i, their root-mean-square variation, σ_i^2 and S_0^2 and E_0 for each metallic element, and 17-31 independent points per dataset. Uncertainties in fitted parameters were calculated using the method of Newville.[19] The refinements achieved good fits for every measured spectrum ending in R values between 1 and 2.5%. To visualize the results,

Figs. 3(a)–3(c) show the EXAFS data and fits for each transition-metal edge. Figures 4(a)–4(c) show the real parts of the Fourier transform of these data.

Since it is rather unusual that copper and silicon share an atomic site, the refinements of the Cu spectrum are discussed in more detail in the following. As for the other elements, the refinements were carried out in R space using a k^2 weight of the dataset. Since the Fourier transformed scattering paths showed excessive overlapping from $R > 3.9$ Å, while the resolution of data became insufficient from this point, the fitting space was limited to 1.7 Å $< R < 3.9$ Å that contained scattering contributions from the first four paths. Hereby, the two first single scattering paths consider the next-neighbor interactions with four Ni ($Cu_0-Ni_{1\_1}-Cu_0$) and six Si atoms ($Cu_0-Si_{2\_2}-Cu_0$). The third contribution is a multiple scattering path resulting from the first and second coordination shell ($Cu_0-Si_{2\_2}-Ni_{1\_1}-Cu_0$), and the fourth path represents a single scattering with the following coordination shell consisting of 12 silicon atoms ($Cu_0-Si_{2\_3}-Cu_0$). Constraints were defined for the parameters δR_i, and σ_i^2 as given in Table I. The resulting changes in the half-path lengths indicate an expansion of the first coordination (Cu–Ni, see Table I) which can be interpreted as the local distortion created by the bigger copper atom, $r=1.38$ Å,[20] sitting on the site of the smaller silicon atom, $r=1.11$ Å.[20] Related to this expansion, the second coordination shell (Cu–Si) shows a small contraction due to the different Cu–Ni and Si–Ni bond lengths. Based on the resulting δR_i values and the structure geometry, the Cu–Ni and Si–Ni bond lengths were calculated. Hereby, the crystal structure gives the following relations between bond lengths and radial distances:

$$d_{Cu-Ni} = R_1 + \delta R_1$$

and

$$d_{Si-Ni} = \sqrt{(R_1 + \delta R_1)^2 + (R_2 + \delta R_2)^2 - 2(R_1 + \delta R_1)(R_2 + \delta R_2)\cos \alpha},$$

where α is the angle between R_1 and R_2, and R_i is the effective path length used in the refinements.

The calculation results in a Cu–Ni bond length of $2.474(8)$ Å and a Si–Ni bond length of $2.337(8)$ Å, which corresponds to a Si–Ni distance of 2.3364 Å in the undistorted structure. Finally, the first and second next neighbors of the undistorted structure are moved into one common coordination shell, and the higher coordination shells show lower deviations. Thus, the refined local distortions, as well as the good fit, support the assumption that copper shares a site with silicon in the $Ni_{0.82}Fe_{0.21}Cu_{0.02}Si_{1.94}$ structure.

Attempts were also made to refine structure models with Cu on an interstitial site or sharing the site with Ni and Fe, but it was not possible to refine these models with resulting R values under 10% [see Figs. 3(d) and 4(d)], which again suggests that Cu occupies the Si site in this compound.

In summary, experimental evidence of the formation of a mixed silicide phase with a fluorite-type structure in silicon samples is presented. The analysis of the precipitates was possible using synchrotron-based μ-EXAFS measurements. Simulation of EXAFS spectra taken on K edges of the transition metals, combined with an analysis of standards synthesized for this study, reveal that the silicide phase has a structure similar to $NiSi_2$ but with mixed occupancies of the Ni and the Si sites. Thus, nickel and iron share the ($4a$) site of the structure, which is reported for various structures because of the similar properties of these elements. On the other hand, copper shares the ($8c$) site with silicon, which is more rare but is physically and chemically feasible. Similarities in the bonding behavior of Cu and Si are theoretically predicted,[21] and the shared site occupancy of these elements within intermetallic compounds, such as Cu_3Si, has been

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