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Model for electron-beam-induced crystallization of amorphous Me-Si-C (Me = Nb or Zr) thin films

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Abstract: We use transmission electron microscopy (TEM) for *in-situ* studies of electron-beam-induced crystallization behavior in thin films of amorphous transition metal silicon carbides based on Zr (group 4 element) and Nb (group 5). Higher silicon content stabilized the amorphous structure while no effects of carbon were detected. Films with Nb start to crystallize at lower electron doses than Zr-containing ones. During the crystallization equiaxed MeC grains are formed in all samples with larger grains for ZrC (~5 nm) compared to NbC (~2 nm). The phenomenon of self-terminating crystallization at 2-5 nm dimension is explained segregation of Si that is expelled from growing metal carbide grains into the surrounding amorphous phase matrix, which limits diffusion of the metal and carbon.

Keywords: transmission electron microscopy (TEM); electron irradiation; radiation effects

I. Introduction

Ternary thin films composed of an early transition metal, silicon, and carbon (Me-Si-C) are used in applications such as protective coatings^[1-3], electrical contacts^[4], printing heads^[5], and solar cells^[6], due to their tribological^[7, 8] and electrical^[9] properties. The thin film properties can be tailored by choice of transition metal and changing the structure through the composition. If magnetron sputtering is used for deposition of Me-Si-C thin films at temperatures below ~700 °C, the structures of the films often range from nanocomposite to amorphous. The structure of these nanocomposites consists of nanosized metal carbide grains (nc-MeC) in an amorphous matrix of SiC or C (a-SiC/a-C)^[4, 10-12]. A general observation is that Si hinders the growth of MeC grains^[13-16]. At higher Si content the Me-Si-C can turn amorphous. An amorphous structure has been reported for several Me (e.g., in the Ti^[17], W^[2, 18], Zr^[3, 13, 19], Nb^[10], Cr^[2], and Mo^[3]) systems. Depending on the choice of transition metal and the deposition conditions, the amount of Si required for the formation of an amorphous structure varies. The Si content is thus important, but how Si disturbs the carbide crystallization and to what extent need further investigation.

We recently deposited Nb-Si-C^[10] and Zr-Si-C^[13] films using the same magnetron sputtering system and deposition parameters except for a slightly higher substrate temperature of 350 °C for Nb-Si-C compared to 300 °C for Zr-Si-C. These two studies show an amorphous structure occurs for Si concentrations above 15 at.% and 25 at.% for Zr-Si-C and Nb-Si-C, respectively. We have also reported that crystallization can be induced by the electron beam during transmission electron microscopy in both amorphous Zr-Si-C and Nb-Si-C^[20]. By varying the dose and energy of the incident electrons the observed crystallization was explained by atomic displacement events. Heating could be ruled out as the main cause of crystallization as *in-situ* annealed (400-

600 °C) samples retained in their amorphous state. This is a higher temperature than expected from the electron beam heating of the samples^[20-22].

These findings highlight the need for great care in imaging these kinds of materials for a correct structure characterization. The possibility to induce crystallization also opens up for a new way to design the materials on the nano-scale. There is, however, no previous systematic study reported to describe the effect of electron-beam irradiation of these materials. Further knowledge on the effect of Si content and C/Me ratio could lead to a deeper understanding of the crystallization mechanism in metal silicon carbides and thus be helpful for the appropriate choice of transition metal and composition when tailoring these materials. In the present study we therefore investigate the role of the Si and C content in order to explain their influence of the stability of amorphous Me-Si-C. We use *in-situ* TEM since it allows observations on the atomic scale. Our findings lead to a model of the crystallization process in which electron irradiation causes the formation of MeC grains and Si segregates to the grain boundaries and the amorphous matrix.

II. Experimental details

Thin film samples deposited from elemental targets onto Si (001) by magnetron sputtering were used for the experiments in this study. Both Nb-Si-C and Zr-Si-C thin films were deposited in the same system under the same conditions except for a slight difference in temperature, 350 °C (Nb) and 300 °C (Zr). A description of the deposition process can be found elsewhere^[10, 13].

TEM cross-sectional specimens were prepared from films deposited on Si(001) substrates. The specimens were mechanically polished down to a thickness of ~50 µm, followed by ion milling in a Gatan Precision Ion Polishing System (PIPS) using 5 keV Ar ions with a final polishing step

with 2 keV Ar ions for 10 min. TEM images and diffraction patterns were then obtained using a FEI Tecnai G2 TF 20 UT with a field-emission gun operated at an acceleration voltage of 200 kV. The crystallization process was performed at ambient temperature with the electron beam focused to a disc with a diameter of ~100 nm. The electron beam current was estimated by measuring the current through the fluorescent viewing screen with the entire beam focused to this area. By also measuring the time the film was exposed to the beam the current density and the electron dose could be calculated.

Elemental maps and Z-contrast images using energy-dispersive X-ray spectrometry (EDX) and scanning TEM (STEM), respectively, were carried out in the double C_s-corrected (image and probe) Linköping Titan³ G2 60-300 HR-TEM.

To determine the crystallized phases the rotational average of several different fast Fourier transforms (FFT) was summed for each sample. The FFTs were filtered with an average background subtraction filter (ABSF) to remove the amorphous component. A description of the ABSF can be found elsewhere ^[23]. The backgrounds from the rotational average were removed manually and the scale was calibrated from images of the single crystal Si substrate. Also selected area electron diffraction (SAED) from larger crystallized areas was used for selected samples to confirm the crystallized phase.

III. Results and discussion

Fig. 1 shows the composition of the samples as determined in references ^[10] and ^[13] for the Nb-Si-C and Zr-Si-C samples, respectively. In each materials system, three different samples are analyzed in order to determine the effects of Si and C content. The Nb-Si-C samples have a

higher Si content compared to the Zr-Si-C samples since this is required to get an amorphous material.

Fig. 2 shows HRTEM images of the Me-Si-C samples in the as-deposited state. The microscopy was made by first focusing the sample in one area, then move the sample to an unexposed area, and quickly record the image. In Fig. 2(a), (b), and (c) the Nb-Si-C samples with composition of $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$, $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$ and $\text{Nb}_{.15}\text{Si}_{.27}\text{C}_{.58}$ are presented, respectively. Fig. 2 (d)-(f) shows the Zr-Si-C samples with composition of $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$, $\text{Zr}_{.43}\text{Si}_{.30}\text{C}_{.27}$ and $\text{Zr}_{.53}\text{Si}_{.20}\text{C}_{.27}$, respectively. All samples are amorphous. Some short range order, such as the area within the indicated circle in Fig. 2(d), can be seen. To ensure that the films are amorphous, low-dose imaging at several places in the film and at different tilting angles were made. This is relevant since grains in some crystal orientations can appear amorphous^[24] and therefore could lead to misinterpretation of the HRTEM results. Together with the information from SAED which show an amorphous structure with only broad rings present, we can conclude that the samples in their as-deposited state are completely amorphous.

Fig. 3 shows images of (a) $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$, (b) $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$ and (c) $\text{Nb}_{.15}\text{Si}_{.27}\text{C}_{.58}$ films after a dose of $4.2 \times 10^8 \text{ e}^-/\text{nm}^2$, which was the lowest dose at which crystallization by certainty could be detected in any of the Me-Si-C samples. The crystallization is most progressed for the sample with lowest Si content (Fig. 3(c)). For the $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$ film in (b), there is a tendency for the crystallization to have started, while the $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$ film in (a) remains amorphous. At a dose of $4.2 \times 10^8 \text{ e}^-/\text{nm}^2$ also all the Zr-Si-C films are still amorphous. In order to observe the effects of increased electron exposure, the samples needed an exposure to a higher dose of $1.9 \times 10^9 \text{ e}^-/\text{nm}^2$. Images of the resulting structure are shown in Fig. 4. Also here the sample with lowest Si content

(Fig. 4(c)) exhibits the highest degree of crystallization. The result that Zr-Si-C need ~4.5 time higher dose than Nb-Si-C before the crystallization process starts clearly shows that Zr-Si-C samples are more stable against crystallization than Nb-Si-C.

In our previous study^[20] we investigated the effect of electron energy, dose, and beam heating. It was found that irradiation of the sample with 80 keV electrons lowered the crystallization rate compared to 200 keV. *In-situ* annealing in TEM of Nb₁₀Si₃₉C₅₁ showed that thermally induced crystallization starts between 400-600 °C. For Zr-Si-C, *in-situ* annealing in X-ray diffractometer in a vacuum furnace (base pressure 5*10⁻⁵ Pa) showed thermally induced crystallization between 500-700 °C^[13]. However, the increase of temperature by the electron beam is not expected to be that high^[20-22]. Thus, we drew the conclusion^[20] that atomic displacement is the main cause of crystallization during electron microscopy studies.

To determine the nanocrystalline fraction is challenging due to varying parameters with focusing conditions and unknown sample thickness. The thickness is of importance since surface effects may affect the crystallization^[25]. The surface atoms are more loosely bonded and sputtering and increased mobility at the surface is therefore possible. Direct measurements of the thickness in TEM are difficult; however, since the samples which are prepared in the same way, always are viewed at the edge of the specimens (i.e., thickness approximately the same), and the initial conditions are the same a qualitative comparison is possible. This study thus only qualitatively separates the crystallization between different samples.

The probability of displacement is related to the maximum transferable energy (E_T) between the colliding electron and atom together with the binding energy in the material. E_T is dependent on

the atomic number and the electron acceleration voltage and an equation for calculating the values of E_T are given by e.g. Egerton et al. ^[25]. The calculated values of E_T using this equation with 200 keV incoming electrons for the materials investigated here are listed in Table I. As seen, more energy can be transferred to lighter elements. Since the atoms are randomly distributed in the amorphous films, the displacement energy (E_d) can have different values for the same element depending on the atomic position ^[26]. An estimation of the displacement energies can be given from displacement energies for the materials in crystalline structure. For the elements investigated here, the corresponding values are listed in Table I. Here we see that it is not likely for Zr or Nb to be displaced while C can easily be displaced. Si can also be displaced since displacement and amorphization has been seen in crystalline Si for electron beam energies above 140 keV ^[27]. Moreover, it is possible for secondary events to occur, where one displaced carbon atom can transfer energy to a Si atom. This has been observed in SiC in which up to 84% of the energy from a carbon atom can be transferred to a Si atom causing displacement ^[28].

When an atom is displaced in an amorphous material, density fluctuations will occur ^[29, 30]. Atoms in the vicinity will then move into the under-dense region to neutralize the density fluctuations. This can explain motion of Me atoms which is needed to form crystallites. Even if the addition of heat from an inelastically scattered electron is not in itself enough to cause crystallization, it could increase the diffusion of atoms in the material leading to faster crystallization. Thus all the elements in the material can move, but only Si and C are likely to be directly displaced by the electron-beam.

Eventually the structure stabilizes and the final state is shown in Fig. 5. All films have equiaxed grains. For the Nb-Si-C samples, the grains are smaller (2-5 nm) compared to the Zr-Si-C

samples (5-7 nm). Fig. 6 shows SAED patterns for the (a) $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$ and (b) $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$ samples together with the results of the normalized sum of the rotational average of several FFT patterns for all the films of Nb-Si-C and Zr-Si-C. Since the shape of the peaks can be affected by the sampling statistics of grains under the area of inspection and background subtraction, especially for the reflections within the band of intensity from the broad peak of the remaining amorphous material, we here focus on the detection of the peaks. In all cases an fcc structure, as indicated in the figures, is the best match to the patterns. This structure was confirmed by measuring the angles and plane distances in the larger Zr-Si-C grains. For the Nb-Si-C and the Zr-Si-C films, the lattice parameter was found to be 4.42 Å and 4.58 Å, respectively. The best match with the measured lattice parameters is from the respective MeCs, (NbC, 4.46 Å (ICDD, PDF card 65-7964), ZrC 4.69 Å (ICDD, PDF card 35-0784)). At continued electron irradiation, displacements will also occur within the MeC grains until a balance is obtained with the relaxation rate of atoms into the crystal structure or, as possible for carbon, to jump between vacant positions in the understoichiometric structure.

The most clearly seen effect is that of the choice of transition metal. All Nb-Si-C films in this study crystallize at lower dose than Zr-Si-C samples regardless of composition. Zr thus gives a more stable amorphous structure than Nb. This can be correlated to the glass-forming ability of the material. Theories for glass-forming ability emphasize the large difference in atomic radius for the constituent elements in the material^[31]. Zr has a larger atomic radius (1.597 Å) compared to Nb (1.456 Å)^[32], which could explain the higher stability of amorphous Zr-Si-C. Another possible explanation can be found from the bond-strength between different atoms in the material. The strength of Me-C bonds decreases by going from period 4 to period 5 in the periodic table^[33], meaning that the Zr-C bonds will be more stable than Nb-C.

The samples with lower Si content crystallize faster. This effective stabilization of the amorphous structure is consistent with observations from nanocomposite Me-Si-C films, where Si disturbs the MeC grain growth. Also the higher amount of strong Si-C bonds, which makes atomic displacements in the material more difficult, could be a reason for the slower crystallization rate with higher Si concentration. Fig. 7 shows the Zr and Si distribution as measured by STEM EDX-mapping for $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$ after irradiation in TEM mode for a dose of $\sim 4 \times 10^{10} \text{ e}^-/\text{nm}^2$. The mapping shows a higher Zr concentration within the grains while Si is concentrated in the surrounding matrix. EELS spectra of the C-K edge summed from STEM EELS mapping over a crystalline grain and an amorphous matrix region of the same sample ($\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$), respectively, are shown in Fig. 8. The edges at 285 and 290 eV are representative for sp^2 and sp^3 bonded C, respectively^[34]. The spectrum indicates that the relative amount of sp^3 C bonds is higher in the matrix phase. This supports the EDX results (cf. Fig. 7) that the matrix is rich in Si, which promotes the formation of sp^3 C bonds^[2, 35]. The seen segregation of Si can be explained by the very low solubility of Si in transition metal carbides^[33], which makes Si atoms become expelled during the formation of MeC grains.

By comparing samples with approximately the same Si content we observe that the carbon content does not significantly influence the crystallization rate for any of the two material systems. This can depend on either that i) carbon is a light and small element and therefore easy to migrate and/or ii) that the MeC_x that forms has at least the wide range of stoichiometry known from phase diagrams ($0.72 < x < 1.0$ ^[32] for NbC_x and $0.61 < x < 1.0$ ^[36] for ZrC_x), such that the C-concentration is of less importance for the formation of MeC.

Fig. 9 shows our proposed model for the crystallization process based on the present results. In the initial crystallization stage the samples have a random distribution of atoms in an amorphous state as shown in Fig. 9(a). During initial electron irradiation, a grain has nucleated in the place marked A in Fig. 9(b). Also shown in b) is a site from which a C atom has been removed through atomic displacement (marked B) creating a density fluctuation that increases the ability of the surrounding Me atoms to move into this empty position and form a carbide crystallite by nucleation and growth. The growing MeC grains require less molar volume compared to the starting amorphous matrix, which increases the length by which atoms from the neighboring matrix need to migrate. This, together with the increase in the concentration of Si at the carbide/matrix interface reduces the crystallization rate. At a certain build-up in Si concentration (Fig. 9(c)), further grain growth is no longer possible because of the yet longer ranges to cover. Possibly, slower interdiffusion of C and Me atoms through the Si-enriched effective tissue phase, also eventually causes crystallization to stop. Effectively the crystallization process becomes self-terminated for grain sizes at or above a few nm.

IV. Conclusions

We have shown that electron-induced crystallization take place in amorphous Me-Si-C systems. Depending on the choice of metal the crystallization starts after different amounts of electron doses. Zr has a more stable amorphous carbide structure than Nb due to its higher glass-forming ability. Si stabilizes the amorphous material and delays the crystallization. The crystallization process and its self-termination is explained by a model, where MeC grains nucleates and grows, but segregation of Si to the carbide/matrix interface eventually hinders the Me and C diffusion.

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For Peer Review

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Figure Captions

FIG. 1. (color online) Composition of the investigated samples in this study.

FIG. 2. HRTEM images from (a) $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$, (b) $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$, (c) $\text{Nb}_{.15}\text{Si}_{.27}\text{C}_{.58}$, (d) $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$, (e) $\text{Zr}_{.43}\text{Si}_{.30}\text{C}_{.27}$, and (f) $\text{Zr}_{.53}\text{Si}_{.20}\text{C}_{.27}$ samples in their as-deposited state. The samples are amorphous with some short-range order as shown with a circle in (d). The insets of the corresponding SAED patterns confirm the amorphous structures.

FIG. 3. Comparison between (a) $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$, (b) $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$, and (c) $\text{Nb}_{.15}\text{Si}_{.27}\text{C}_{.58}$ samples at the lowest dose ($4.2 \times 10^8 \text{ e}^-/\text{nm}^2$) at which crystallization could be detected in any of the Nb-Si-C samples. The insets show the center part of the FFT of the corresponding images.

FIG. 4. Comparison between (a) $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$, (b) $\text{Zr}_{.43}\text{Si}_{.30}\text{C}_{.27}$, and (c) $\text{Zr}_{.53}\text{Si}_{.20}\text{C}_{.27}$ samples at the lowest dose ($1.9 \times 10^9 \text{ e}^-/\text{nm}^2$) at which crystallization could be detected in any of the Zr-Si-C samples. The insets show the center part of the FFT of the corresponding image.

FIG. 5. The final state of (a) $\text{Nb}_{.36}\text{Si}_{.46}\text{C}_{.18}$, (b) $\text{Nb}_{.10}\text{Si}_{.39}\text{C}_{.51}$, (c) $\text{Nb}_{.15}\text{Si}_{.27}\text{C}_{.58}$, (d) $\text{Zr}_{.52}\text{Si}_{.30}\text{C}_{.18}$, (e) $\text{Zr}_{.43}\text{Si}_{.30}\text{C}_{.27}$, and (f) $\text{Zr}_{.53}\text{Si}_{.20}\text{C}_{.27}$ samples after a longer time of irradiation. ($\text{Zr-Si-C} \sim 4 \times 10^{10} \text{ e}^-/\text{nm}^2$, $\text{Nb-Si-C} \sim 2 \times 10^{10} \text{ e}^-/\text{nm}^2$) at which the structure have stabilized. The insets show the center part of the FFT of the corresponding image.

FIG. 6. (color online) SAED (left) and rotational average from FFT (right) for crystallized (a) Nb-Si-C and (b) Zr-Si-C. All patterns can be matched to the marked NaCl-structure of respective MeC.

FIG. 7. (color online) STEM HAADF image, with corresponding elemental EDX-map of Zr and Si. The concentration of Si is seen to be higher in the matrix phase while Zr is mainly present within the crystallites.

FIG. 8. (color online) EEL spectrum of C K-edge for from a crystalline grain and the matrix phase of the $Zr_{.52}Si_{.30}C_{.18}$ after electron irradiation. The edges seen at 285 and 290 eV indicate a higher amount of relative sp^3 C bonds in the matrix phase.

FIG. 9. Proposed model for crystallization (a) as-deposited, (b) after initial electron irradiation, which initiates the crystallization process, and (c) final state. In (b) A marks a place of initial crystallization and B a density fluctuation caused by atomic displacement. White areas surrounding the MeC grains are to illustrate a less dense matrix.

TABLE I. The maximum transferable energy (E_T) at 200 keV, together with the displacement energy (E_d).

Element	E_T [eV]	E_d [eV]
Nb	5.64 ^b	24 ^a
Zr	5.74 ^b	74-121 ^d
C	43.7 ^b	20 ^c
Si	18.7 ^b	13-25 ^d , 35 ^c

^a From Table 4.3 in ^[37], ^b Calculated from eq. 2 in ^[25], ^c ^[28], and ^d ^[27].

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