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Beam-induced crystallization of amorphous Me-Si-C (Me = Nb or Zr) thin films during transmission electron microscopy

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Abstract

We report that an electron beam focused for high resolution imaging rapidly initiates observable crystallization of amorphous Me-Si-C films. For 200-keV electron irradiation of Nb-Si-C and Zr-Si-C films, crystallization is observed at doses of $\sim 2.8 \cdot 10^9$ and $\sim 4.7 \cdot 10^9$ e⁻/nm², respectively. The crystallization process is driven by atomic displacement events, rather than heating from the electron beam as *in-situ* annealing (400-600 °C) retains the amorphous state. Our findings demand a critical analysis of alleged amorphous and nanocrystalline ceramics including reassessing previous reports on nanocrystalline Me-Si-C films for possible electron-beam-induced crystallization effects.

Introduction

For structural characterization of nanocrystalline and amorphous materials, imaging by transmission electron microscopy (TEM) with high spatial resolution and elemental contrast is a standard technique. It is therefore of general interest for the community of material science to know if their materials are susceptible for the artifacts the energetic electron irradiation during TEM studies may evoke ^[1, 2]. The artifacts have been reported both as amorphization of crystalline materials ^[3, 4] and crystallization of amorphous materials ^[5, 6], depending on electron energy, dose, and the type of material. These sample artifacts may be due to processes such as atomic displacement, radiolysis, and sample heating ^[1, 2, 7].

An important class of materials is the metal carbides. These have wide stoichiometry ranges and exhibit several crystal structures that often form nanocomposites when rich in carbon. More elements are added to tailor the materials for, e.g., tribological or electrical applications ^[8-11]. For example, thin films of the Ti-Si-C system can be grown with a nanocomposite structure consisting of TiC crystallites embedded in an amorphous matrix of SiC and C ^[12-14]. Amorphous (glass-like) structures are also reported to form in Me-Si-C systems (e.g., for the metals Me = Ti ^[15], Zr ^[16], Mo ^[17], and W ^[18]). For TEM characterization of these complex-structure materials, it is essential to find not only imaging conditions, but also sample preparation methods that allow characterization of the true nature of the material. Correspondingly, one should elucidate any electron-beam/sample interaction including possible crystallization.

Here, we report the effects of electron beam interactions with dc magnetron sputtered Me-Si-C thin films with amorphous structure during TEM analysis. Since the only observable interactions are under high resolution (HR-)TEM conditions, this study uses the technique both

to induce artifacts and observe them. The metal (Me) was selected from group 4 (Zr) and group 5 (Nb) in the periodic table. We separate between different damage effects by imaging the sample at different current densities and acceleration voltages. The effects of sample heating by *in situ* annealing are also investigated. Comparing the nanocrystalline fraction from HRTEM images can be challenging due to e.g. unknown sample thicknesses and different defocusing conditions. However we are here able to qualitatively separate the different damage effects. The results show that the amorphous phase of both material systems is unstable to exposure of the HRTEM electron beam, which induces MeC crystallization. Low-dose electron exposure, however, offers a way to better determine their structure.

Experimental

Thin films of Me-Si-C (Me = Nb or Zr) were deposited from elemental targets using dc magnetron sputtering in an Ar discharge. A detailed description of the deposition process, together with compositional and structural characterization for Nb-Si-C and Zr-Si-C can be found in ^[19] and ^[20], respectively.

Cross-sectional specimens were obtained by mechanically polishing down to ~50 μm followed by ion milling (at 5° incidence angle) in a Gatan Precision Ion Polishing System (PIPS) using 5 keV Ar^+ ions. As a final step the samples were polished with 2 keV Ar^+ ions. Ion-milling involves potential damage to the material. For the present class of materials, Lewin et al. ^[21] found that etching Ti-Me-C (Me=Al, Fe, Cu, Pt or Ni) films with 4 keV Ar^+ ions altered the chemical bonding observed in XPS. The same energy-range (~1-5 keV) is used during ion-milling in the TEM sample preparation. Thus, in order to exclude any possible damage effects from ion radiation, the small angle cleavage technique (SACT) ^[22] was used on the $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ sample. This sample was polished down from the substrate side to a thickness of ~70 μm followed by cleavage at a small angle (~17°) to the edge, creating a very thin region

at the interface. The technique guarantees radiation damage free samples, albeit relatively small regions will be electron transparent ^[23].

Transmission electron microscopy experiments were carried out in a FEI Tecnai G2 TF 20 UT instrument with a field-emission gun operated at acceleration voltages of 200 and 80 kV. The electron beam current was estimated by measurement of a focused beam on the fluorescent viewing screen. By setting the spot size and the exposure time, the current density and the electron dose could be calculated.

For the annealing experiment a heating sample holder was used. First the set-point temperature was put to 350 °C and the held until the drift of the sample had stabilized. The temperature was then kept for additional 20 min before an image was acquired. This procedure was then repeated for new set-points of 400 and 600 °C. For the 600 °C heating experiment the sample had to be cold down to 400 °C before an image could be taken due to vibrations from external water-cooling of the rest of the sample holder.

Results and discussion

Figure 1 shows TEM images of (a) and (b) $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$, and (c) $\text{Zr}_{0.43}\text{Si}_{0.30}\text{C}_{0.27}$ samples from direct imaging by rapid beam shift to a previously non-exposed area (i.e. the as-deposited state). The samples in (a), (c), are prepared with ion-milling, while the sample in (b) is prepared with SACT. All specimens exhibit amorphous structures with only some short-range ordering present. Since no considerable difference can be found between the SACT and ion-milled sample, we conclude that ion-milling during sample preparation does not affect the samples significantly. The amorphous structure is also supported by selected area electron diffraction (not shown) taken over a larger area of the film. Hence both materials are amorphous in their as-deposited state.

Crystallization of our samples started during HRTEM imaging. Quantitative comparisons between crystallized specimens can be difficult since it acquires knowledge of specimen thickness and some crystallites might also appear amorphous due to their orientation. However, if all the specimens are prepared in the same way and the images are taken at the edge of the films (i.e. thickness approximately the same), the initial conditions are the same and a qualitative comparison is possible. In this article we thus qualitatively determined the amount of crystallization by comparing the number of observable crystalline grains formed and their size between different experimental treatments of the specimens. Figure 2 shows the structure evolution of the $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ film from (a) as-deposited state to (b) and (c) different beam currents of 1.2 nA and 9.1 nA, respectively, for the same electron dose of $\sim 2.8 \times 10^9 \text{ e}^-/\text{nm}^2$. Both (b) and (c) show a similar state of crystallization consisting of equiaxed crystallites with a diameter of $\sim 2\text{-}5 \text{ nm}$. The diffraction patterns from the crystallized grains appearing in the FFT (insets Fig. 2(b) and (c)) agree well with that expected for an fcc structure. The best match for the lattice parameter ($4.44 \text{ \AA}$ with standard deviation of $\pm 0.03 \text{ \AA}$ as calculated from the micrograph) is NbC ($4.46 \text{ \AA}$ [ICDD, PDF card 65-7964]). The calculated lattice parameter is within error of the measurement, but the fact that the measured lattice parameter is smaller indicates that the crystallized NbC is understoichiometric on C. The similar state of crystallization in Fig. 2(b) and (c) shows that the crystallization process is dose dependent. For $\text{Zr}_{0.43}\text{Si}_{0.30}\text{C}_{0.27}$, the same dose ($\sim 2.8 \times 10^9 \text{ e}^-/\text{nm}^2$) shown in Fig. 3(b), does not affect the film as much as in the Nb-Si-C case. Only one grain in the thinnest part of the specimen (indicated by arrow) can be observed. After a longer exposure time (dose $\sim 4.7 \times 10^9 \text{ e}^-/\text{nm}^2$) also the $\text{Zr}_{0.43}\text{Si}_{0.30}\text{C}_{0.27}$ crystallized (Fig. 3(c)). Similar to the $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ film, the crystallites are equiaxed with a diameter of $\sim 2\text{-}5 \text{ nm}$. The structure (fcc) and the calculated lattice parameter ($4.70 \text{ \AA}$ with standard deviation of $\pm 0.02 \text{ \AA}$) are in agreement to that of ZrC (lattice parameter $4.69 \text{ \AA}$ [ICDD, PDF card 35-0784]). A reason for the need of higher dose-rates in the

crystallization process of Zr-Si-C compared to Nb-Si-C could be the larger atomic radius of Zr, which from metallic glasses is known to stabilize the amorphous structure when mixed with elements of smaller atomic radii ^[24].

Heating of the sample can be excluded as the main explanation for the crystallization based on the following annealing experiments. The electron-beam heating depends on several parameters of the sample such as, thermal conductivity and thickness, as well as properties of the beam, e.g., current and beam radius. To first order, the temperature increase can be approximated as proportional to the beam current through the specimen ^[25]. Williams and Carter ^[7] give general examples of this for materials with different thermal conductivity. It was shown that at a beam current in the order of 10 nA (this work), the temperature rise is not expected to be higher than 100 K even for an insulator (thermal conductivity 0.1 W/(m*K)). Figures 4(a) and (b) show TEM micrographs of the Nb_{0.10}Si_{0.39}C_{0.51} specimen after annealing for 20 min at 400 °C and 600 °C, respectively. At 400 °C no evidence of crystallization can be seen, but at 600 °C small crystalline grains have started to form. This crystallization process is, however, much slower compared to the beam-exposure experiment (cf. Fig. 2).

Also radiolysis can be excluded by the following experiment and line of arguments. In this process an inelastic scattered electron excites an electron in the material to make an interband transition. Defects formed in the following recombination process can lead to increased atom mobility and induce density fluctuations, which may induce crystallization ^[6] Radiolysis depends on electron-electron interactions, which increase with decreased acceleration voltage. Figure 4(c) and (d) shows the Nb_{0.10}Si_{0.39}C_{0.51} sample irradiated with the same dose but at 80 keV and 200 keV electrons, respectively. At 80 keV the crystallization is remarkably reduced. This contradicts that the crystallization process is caused by radiolysis.

Instead atomic displacement is suggested to cause crystallization. Displacement is due to elastic scattering and occurs when the transferred energy (E_T) is larger than the displacement energy (E_d) for an atom. More energy can be transferred to the lighter elements and at higher beam electron acceleration voltages ^[1]. As seen in Fig. 4 (c) and (d), higher electron energy causes more crystallization for the same dose. Since thermal heating is excluded, this indicates that atomic displacement is the main cause for the crystallization. Further investigations are needed to determine which element or elements that are displaced. It is nevertheless more likely to be C and/or Si since these elements are lighter and can gain more energy from an displacement event. The electron beam-induced atomic displacements will thus cause additional or alternative disorder in the amorphous material. These defects can be seen as density fluctuations and the atomic reconfiguration to neutralize the fluctuations, can lead to the formation of crystalline clusters ^[6].

Conclusions

Amorphous Me-Si-C (Me = Zr, or Nb) thin films made by magnetron sputtering tend to crystallize due to electron irradiation during TEM investigations. Thereby, metal carbide crystallites form in both Nb-Si-C and Zr-Si-C. The crystallization is primarily caused by atom displacements.

These findings emphasize the need for great care in imaging this kind of materials for a correct structure characterization. This is preferably done by low-dose electron microscopy. Finally, in light of the here demonstrated electron-beam induced crystallization, there is a need to revisit and critically assess literature on nanocrystalline carbide-based nanocomposites, in particular when TEM results appear to contradict characterization by other techniques such as XRD and Raman spectroscopy. Furthermore, possible electron-beam induced crystallization needs to be

considered also for other similar amorphous materials, such as in the Me-Si-N or Me-Si-B systems.

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(a)

(b)

(c)

FIG. 1. HRTEM images of the as-deposited $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$, prepared by ion milling and SACT in (a) and (b), respectively, (c) $\text{Zr}_{0.43}\text{Si}_{0.30}\text{C}_{0.27}$ prepared by ion milling.

(a)

(b)

(c)

FIG. 2. HRTEM images of the $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ film in as-deposited state (a), and (b) and (c) after exposure to a dose of $\sim 2.8 \times 10^9 \text{ e}^-/\text{nm}^2$ for different beam currents of 1.2 nA and 9.1 nA, respectively.

(a)

(b)

(c)

FIG. 3. HRTEM images with corresponding FFT insets of the $\text{Zr}_{0.43}\text{Si}_{0.30}\text{C}_{0.27}$ film in an as-deposited state, (a), and, after exposure to a dose of $\sim 2.8 \times 10^9 \text{ e}^-/\text{nm}^2$, (b), and, $\sim 4.7 \times 10^9 \text{ e}^-/\text{nm}^2$, (c). The arrow in (b) marks a small crystalline grain.

FIG. 4. HRTEM images with corresponding FFT insets (a) and (b) $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ thermally heated to 400 °C and 600 °C, respectively. (c) and (d) $\text{Nb}_{0.10}\text{Si}_{0.39}\text{C}_{0.51}$ exposed to irradiated electrons with an acceleration voltage of 80 kV and 200 kV, respectively.

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