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Atomic transport in metastable compounds: Case study of self-diffusion in Si-C-N films using neutron reflectometry

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The investigation of atomic mobilities in transient metastable phases is a challenging task in diffusion science. For amorphous silicon carbonitrides we identified a transient metastable bonding configuration by Fourier-transform infrared spectroscopy on samples annealed in a defined time-temperature domain. We demonstrate that it is possible to determine nitrogen self-diffusivities in this state using neutron reflectometry. The results revealed that the diffusion experiments on this system are feasible only if very short diffusion lengths on the order of 1 nm and very low diffusivities can be measured, as it is the case for neutron reflectometry technique applied in our studies.

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A large number of materials with interesting electronic, optic, and catalytic properties[1,2] used in everyday life are actually not thermodynamically stable but only metastable.[1–3] Metastable materials are located at a relative minimum of Gibbs free energy.[2–4] Supply of thermal energy will result in dissociation or transformation of the metastable state into a more stable state.[2–4] Often metastable compounds correspond to transition states that occur when a change in phase, crystal structure, or chemical bonding takes place by annealing in a defined time-temperature domain. Hence, the observation time scale becomes an additional parameter in the phase diagram, in addition to temperature, pressure, or concentration.[3,4] The kinetic and atomic transport properties of metastable phases are of recent interest in various materials ranging from solid[2–10] to soft[11,12] matter. We show that neutron reflectometry (NR) can be a suitable experimental method to investigate atomic transport in metastable transition states.

An interesting object of study are silicon carbonitrides (Si-C-N), a class of advanced multifunctional high-temperature materials[8–10] with applications ranging from wear-protection and corrosion-resistant hard coatings[13] over wide-band-gap blue-ultraviolet optoelectronic devices,[14] sensors,[14] and magnetic devices[15] to diesel trapping, biomedical implants,[16] and sand erosion protection.[17] They can be produced by a variety of methods such as polymer pyrolysis,[8,9] laser deposition,[18] ion implantation,[19] and magnetron sputtering[20,21] in the form of bulk materials and thin films. After synthesis Si-C-N materials are generally in a complex amorphous state, showing interesting features such as nanometer-scale phase separation[22] or transitions to new ternary crystalline compounds[9,10,23] and also metastable phases.

Due to the occurrence of nonequilibrium and metastable phases in Si-C-N, the atomic mobility (or the related self-diffusivity) plays an important role for the formation and stability of certain phases of this material, as well as for phase transformations and microstructural modifications.[4,23,24] Recently, Golczewski[4] presented a study where it was shown that, for the phase diagram of amorphous Si-C-N ceramics, the Gibbs energy becomes directly dependent on time due to atomic kinetics, emphasizing the importance of atomic transport measurements.

So far, there exist a limited number of diffusion studies for Si-C-N,[25,26] but it was not possible to detect self-diffusivities in transient metastable compounds, which are, e.g., distinguished by special bonding configurations. When applying classical tracer methods[27] (radioactive or stable) for the determination of diffusivities, the annealing time has to be considerably shorter than the lifetime of the metastable state at this temperature. For a given diffusivity D and some short annealing times t, the diffusion lengths $d=\sqrt{2Dt}$ that have to be detected will also be small. Neutron reflectometry[28] is an advanced method to determine self-diffusivities.[29–34] It has the advantage over other methods to be nondestructive and is able to determine even subnanometer diffusion lengths.[32–34] Following the annealing time dependence of bonding configurations by Fourier-transform infrared spectroscopy (FTIR) we identified a metastable transient state in the system Si-C-N and applied neutron reflectometry to quantify nitrogen diffusivities in this state. From diffusion studies on similar Si-(B-)C-N materials produced by polymer pyrolysis and investigated by secondary ion mass spectrometry, it is known that all three species diffuse approximately with the same diffusivity[35] and, hence, nitrogen can be seen as a characteristic atom in describing the overall diffusion behavior.

High-purity Si-C-N films were deposited on silicon wafers using rf magnetron cosputtering following the procedure described in Ref. 21. For the diffusion experiments isotope multilayers were produced containing ten $\mathrm{SiC}_x\,{}^{15}\mathrm{N}_y(16\ \mathrm{nm})/\mathrm{SiC}_x\,{}^{14}\mathrm{N}_y(16\ \mathrm{nm})$ double layers. The composition of the as-deposited film was determined to be $\mathrm{Si}_{2.0}\mathrm{C}_{1.1}\mathrm{N}_{3.6}$ by Rutherford backscattering spectrometry using a 2.0 MeV ${}^4\mathrm{He}^+$ ion beam focused to 0.5 mm in diameter. Considering the backscattering angle of 165°, the 1 mm aperture mounted at the surface barrier detector, the beam current of 10 nA, the charge of 50 μC, and the accuracy in the stopping cross section values, the accuracy of the measurements is calculated to 5%. Annealing was carried out at 867 °C in a conventional tube furnace in nitrogen at 970 mbar. After annealing the samples were cooled down to room temperature and investigated by FTIR and/or NR. FTIR was carried out with a evacuated ($p < 1$ mbar) Bruker IFS 66v/s spectrometer, which was equipped with a Globar infrared source and a DLTAGS detector. FTIR spectra of Si-C-N films were recorded with 2 cm^{-1} resolution in a reflection geometry and corrected for the substrate contribution. Diffusion studies with NR were conducted at the Swiss Spallation Neutron Source (SINQ), using the time-of-flight apparatus for multi option reflectometry (AMOR). At incoming neutron wavelengths between 0.2 and 0.9 nm the reflectivity pattern was measured at incident angles of 0.5° and 0.8°, respectively. The approximate duration of the measurement around the Bragg peak was about 2 h.

X-ray diffractometry measurements revealed that the as-deposited and annealed films used in this study are amorphous. In order to recognize particular C-N, Si-N, and Si-C functional groups and to follow their annealing time dependence we applied FTIR. The FTIR spectra in Fig. 1 of an as-deposited amorphous Si-C-N film and of the same film annealed at 867 °C exhibit three vibrational bands. The band visible between 800 and 1000 cm^{-1} has been attributed in Refs. 20 and 36 to Si-N bonds including SiN_4 tetrahedral vibrations at 840 cm^{-1}. Absorbance at Si-C bonds should appear[20,37] as a strong peak between 800 and 720 cm^{-1}. Since in this wave number range the absorbance is possibly caused only by the tail of the SiN_4 tetrahedral bands, the carbon atoms in the as-prepared Si-C-N film are likely bound to nitrogen only. This is in agreement with recent investigations[38] on the bond affinity of Si, C, and N in Si-C-N materials, where it was shown that the affinity of carbon to nitrogen is higher than to silicon. The weak band between 1400 and 2000 cm^{-1} can arise from[10] C≡N, C=N, C-N or even of C=C bonds due to the presence of nitrogen.[20,39] The wave number of the strong band centered at 2240 cm^{-1} is indicative for cyanamide N-C≡N vibrations.[10] On the other hand, the asymmetric stretching vibration of carbodiimide N=C=N groups would give rise[10,19,20] to a band near 2152 cm^{-1}. Due to the broad distribution of single bonds in amorphous materials it is not possible to unambiguously decide which of the two bonding configurations, N=C=N or N-C≡N, is present. However, in comparison to the more symmetric double bond N=C=N, the asymmetry of the cyanamide (N-C≡N) configuration is more inflective on its further bond to a Si atom[40] and, therefore, better suited to fit in an amorphous Si-C-N network.

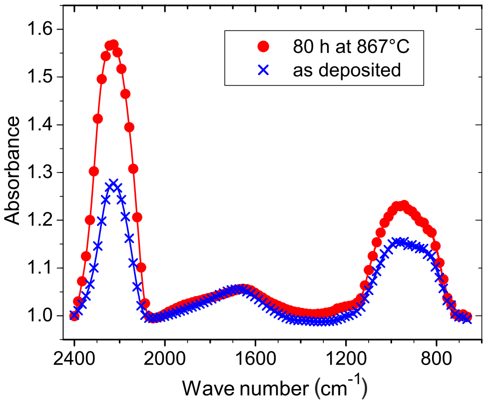

FIG. 1. (Color online) FTIR spectrum of as-deposited and annealed Si-C-N.

From a close inspection of Fig. 2, it is obvious that the integrated absorbance of the vibrational bands at 2240 cm^{-1} and around 900 cm^{-1} depends on the annealing time. For annealing times up to 2 h at 867 °C, there is a rapid increase of the adsorbance at 2240 and 900 cm^{-1} (region A in Fig. 2). Region A in Fig. 2 is followed by a plateau with nearly constant intensity for annealing times of about 100 h (region B). Here, the numbers of N-C≡N and/or N=C=N bonds and of Si-N bonds corresponding to SiN_4 tetrahedra remain constant. Additional annealing up to 900 h leads to a decrease in N-C≡N and/or N=C=N bonds (region C in Fig. 2). Due to these findings we relate region B to a metastable transient state.

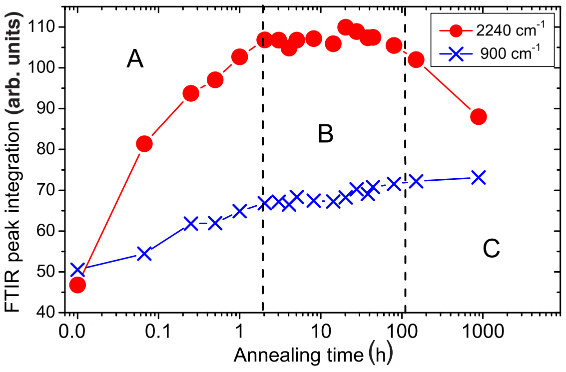

FIG. 2. (Color online) Integrated FTIR intensity of the bands at 2240 cm^{-1} (marked with dots) and around 900 cm^{-1} (marked with crosses) after subsequent anneals at 867 °C (lines are a guide to the eye).

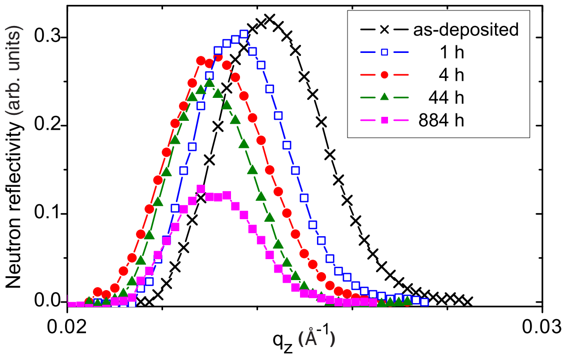

FIG. 3. (Color online) Decrease in first-order Bragg peak after annealing the Si-C-N isotope multilayer at 867 °C (lines are a guide to the eye).

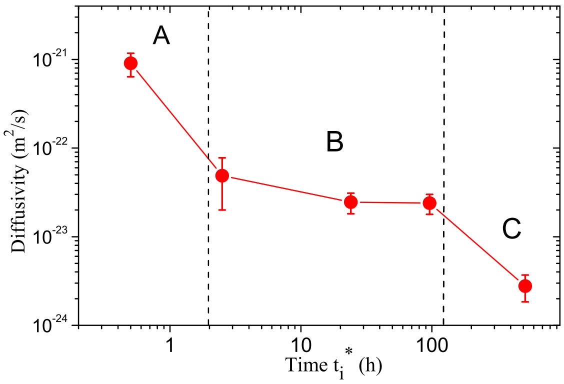

FIG. 4. (Color online) Average nitrogen self-diffusivity as a function of time, according to Eq. (1) (lines are a guide to the eye).

The occurrence of the three regions of Fig. 2 as a function of annealing time can be interpreted as follows: after deposition, the Si-C-N films are expected to be in a rather disordered state. The atoms are randomly distributed with a low fraction of chemical order in form of N-C≡N and/or N=C=N and $\mathrm{SiN_4}$ bonding configurations, respectively. In region A, chemical short-range order increases with annealing time until a transient metastable state is reached in region B. From these results and recent literature[9,10] the structure of the material in the metastable state can be visualized as silicon nitride tetrahedra which are connected by N-C≡N and/or N=C=N bonds to a three-dimensional amorphous network. In region C the number of N-C≡N and/or N=C=N bonds is reduced and the material is presumably dissociating to amorphous silicon nitride, a residual carbon phase and nitrogen gas. Detailed measurements based on Raman spectroscopy are in progress.

The results of our neutron reflectometry measurements are illustrated in Fig. 3. For the study of nitrogen diffusion, chemically homogeneous isotope $[\mathrm{SiC}\,^{15}\mathrm{N}(16\text{ nm})/\mathrm{SiC}\,^{14}\mathrm{N}(16\text{ nm})]_{10}$ multilayers were used.[32] Due to the periodic arrangement of isotope enriched single layers a Bragg peak is formed in the reflectivity pattern by the reflection of neutrons at isotope interfaces.[32] As a consequence of the isothermal annealing at 867 °C the Bragg peak decreases, which is caused by isotope interdiffusion across interfaces. For annealing times t_i $(i=1,2,\ldots,5)$ of 1, 4, 44, 148, and 884 h and $t_0=0$ h the average diffusivity at $t_i^\star=t_i+\Delta t_i/2$ with $\Delta t_i=t_{i+1}-t_i$ can be determined according to

$$D(t_i^\star)=\frac{l_b^2}{8\pi^2 n^2\Delta t_i}\ln\frac{I(t_i)}{I(t_{i+1})}, \tag{1}$$

where $I(t_i)$ and $I(t_{i+1})$ are the intensities of the nth-order Bragg peak at times t_i and t_{i+1}, D is the diffusivity, and l_b is the bilayer periodicity.[31–34,41] Figure 4 presents the obtained diffusivities as a function of $t_i^\star$.

It is obvious from Fig. 3 that the Bragg peak not only decreases in intensity, but also shifts to lower q_z values up to 4 h of annealing. This shift indicates an increase in the Si-C-N film thickness, corresponding to a decrease in the mass density of about 9%. As a result we see that the formation of cyanamide (or carbodiimide) functional groups in region A of Fig. 2 is accompanied by a continuous mass density modification. In regions B and C the mass density remains constant.

From a comparison of Figs. 2 and 4 a close correlation of the determined diffusivities and the integrated FTIR intensity is observed. In regions A and C, where the number of specific bonds changes, the diffusivities strongly decrease during annealing with increasing annealing time by more than one order of magnitude. In the metastable region B the diffusivities are constant within error limits for annealing times between 2 and 100 h. Consequently a diffusivity of 3×10^{-23} m^2/s can be attributed to the metastable state.

Figure 5 presents the corresponding diffusion lengths calculated by means of the relation

$$d(t_i^\star)=\sqrt{2D\Delta t_i}. \tag{2}$$

In order to determine the three diffusivities in region B, diffusion lengths of 1–3 nm have to be measured. Consequently, the diffusivity in the metastable region B can be determined by neutron reflectometry, but not by (i) techniques such as conventional tracer methods, which can only detect minimum diffusion lengths of 10–20 nm, or by (ii) techniques such as quasielastic neutron scattering or nuclear magnetic resonance relaxometry, which are not able to determine low diffusivities below $D=10^{-16}$ m^2/s.

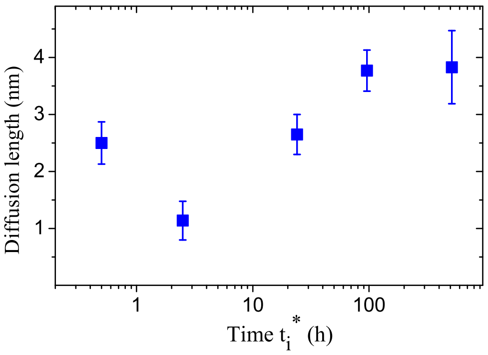

FIG. 5. (Color online) Self-diffusion lengths determined according to Eq. (2).

In conclusion, we have shown that self-diffusivities in transient metastable bonding configurations can be determined by neutron reflectometry. For amorphous Si-C-N a metastable state distinguished by a constant number of N-C≡N and/or N=C=N bonds could be reached after isothermal annealing for 2 h at 867 °C, which is stable for about 100 h of additional annealing. Further annealing leads to dissociation. The capability of the neutron reflectometry technique to detect diffusion lengths on the order of 1 nm allowed us to attribute a specific diffusivity to this metastable transition state.

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