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Proposal to the ISOLDE Scientific Committee (ISC)

Self-Diffusion of Carbon and Nitrogen in the Amorphous Ceramics Si_{26}C_{41}N_{33} and Related Materials

Stuttgart–ISOLDE Collaboration

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1. Introduction

It is intended to measure the self-diffusivities of carbon and nitrogen in amorphous covalent $\text{Si}_{26}\text{C}_{41}\text{N}_{33}$ (and, in a later stage, in related materials such as amorphous carbon and amorphous $\text{Si}_3\text{N}_4$). This extraordinary system has been chosen as a subject of investigation because of both a technological and a scientific reason, as will be explained in some detail in what follows.

![Diagram of production route](image)

Fig. 1. Production route of ceramics from polymeric precursors.
Technological Aspects. A challenging technological objective is the production of crystalline ceramics from polymeric precursor substances [1]. The production route of this is shown schematically in Fig. 1. An important step in this procedure is a pyrolytic treatment at 1050°C that results in monolithic amorphous covalent ceramics composed of Si, C, N, and sometimes B. In the present work the amorphous ceramics to be investigated is \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \). Subsequent thermal treatments above the pyrolysis temperature lead to the final product, a crystalline ceramic.

The transition from the intermediate amorphous state of \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \) to its final crystalline ceramic phase is diffusion-controlled. Therefore, it is of vital technological importance to know the self-diffusivities of the components Si, C, and N.

In a previous experiment at the mass separator of Bonn University the radioactive isotope \(^{71}\text{Ge} \) has been implanted into amorphous \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \), and then, using the radiotracer technique, its diffusivities have been studied at various temperatures and after different pre-annealing treatments of the amorphous matrix (Section 3.1). This has been done since, as is well-known, in several covalently bonded materials the diffusivity of Ge differs only weakly from that of Si, i.e., in such materials Si diffusion may be "simulated" by Ge diffusion. (For instance, self-diffusion in crystalline Si has been simulated by the diffusion of Ge isotopes [2].) This is of great importance since there is no radioisotope of Si available with a half-life that is suitable for radiotracer diffusion studies, in marked contrast to what is true for Ge.

Obviously, a remaining high-priority task is the measurement of the self-diffusivities of C and N in amorphous (and, certainly, later also in crystalline) \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \). As mentioned above, right this is the content of the present proposal (Sections 4 and 5).

Basic-Research Aspects. An important objective in solid-state physics is the understanding of the mechanisms of diffusion in amorphous covalent materials. Systematic investigations aiming at this have so far been restricted to amorphous elemental semiconductors (a-Si, a-Ge, and a-Si–Ge alloys) and preferentially to transition-metal diffusers [3]. A great disadvantage of these materials is their fairly low temperatures of crystallization. (For instance, a-Si already crystallizes at about 630°C, this temperature may be reduced by so-called metal-induced crystallization to 150°C if a-Si is brought in contact with metals [4].) At these low temperatures, diffusion studies are extremely difficult and, in part, even impossible, since solid-state diffusivities decrease with decreasing temperatures and thus are quite low in the temperature regimes of existence of a-Si and a-Ge. In the case of transition-metal diffusers their low solubility at low temperatures adds further difficulties to studies of their diffusivities. Self-diffusion measurements on a-Si and a-Ge are not doable at all, since below the crystallization temperatures the self-diffusivities are unmeasurably small. All these difficulties do not exist in the case of the amorphous ceramics introduced above. So in amorphous \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \) crystallization requires temperatures of about 1400°C, and even at temperatures as low as about 800°C Ge diffusion is easily measurable (Section 3.1). These facts make amorphous ceramics to outstanding candidates for diffusion studies in amorphous covalent solids.

The prime objective in diffusion science is the understanding of the mechanisms of self-diffusion. Concerning amorphous \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \), the self-diffusion of Si has already been simulated by the diffusion of \(^{71}\text{Ge} \) (see above and Section 3.1). Thus concerning diffusion in this material the remaining high-priority tasks are self-diffusion measurements of C and N.

In analogy to other solids for which the mechanisms of diffusion are well-known (crystalline metals and semiconductors), it is expected that in \( \text{Si}_{26}\text{C}_{41}\text{N}_{33} \) self-diffusion occurs via indirect mechanisms involving intrinsic defects while foreign metal atoms undergo direct interstitial-like diffusion. Whereas indirect diffusion requires high activation enthalpies, a characteristic feature of direct diffusion mechanisms is their comparatively small activation
enthalpies. In order to exploit this empirical rule when searching for the diffusion mechanisms in amorphous Si$_{26}$C$_{41}$N$_{33}$, our first diffusion experiments on amorphous Si$_{26}$C$_{41}$N$_{33}$ also included Au as a representative of the metal-atom diffusers (Section 3.2).

2. Experimental Techniques and Experience

The experimental method most frequently applied in diffusion studies at our laboratory is the radiotracer technique combined with serial sectioning of the specimens [5]. In a routine experiment the radiotracer atoms whose diffusivity is to be studied are deposited in a thin layer of less than 1 nm on the specimen surface either electrochemically or by vapour deposition. The next step is diffusion annealing at the temperature at which the diffusion coefficient shall be measured. Depending on the penetration depth $\Delta$ of the tracers, the subsequent sectioning of the specimen is done by high-precision grinding ($\Delta \approx 10-100$ $\mu$m) or (Ar$^+$-)ion-beam sputtering ($\Delta \leq$ about 500 nm). In the case of ion-beam sputtering the sputtered-off material is collected on a foil which is discontinuously wound up like a film in a camera. Then the specific radioactivities of the various foil segments, which correspond to different penetration depths of the tracers in the specimen, are measured with a Ge(Li) or NaI $\gamma$-spectrometer or with a liquid-scintillation $\beta$-spectrometer depending on the nature of the radioisotopes.

In a modification of the radiotracer technique the radioactive atoms are implanted into the specimens to depths ranging from 20 nm to 100 nm. In this way, the radiotracer atoms are deposited beyond unwanted diffusion barriers at the specimen surface [6]. Depending on the kind of implanted radioactive ions, the implantations may be done at the mass separator of Bonn University or at ISOLDE. As will be reported in Section 3, in our previous investigations of the diffusion of $^{71}$Ge and $^{195}$Au in amorphous Si$_{26}$C$_{41}$N$_{33}$ the implantations have been done at these facilities, respectively.

In our team a large body of experience with diffusion studies of the kind described above has accumulated. In particular, systematic investigations of the diffusion in amorphous metallic alloys [5, 7] both in the glassy and in the undercooled liquid regime, in both crystalline [8] and amorphous [3] elemental semiconductors, in quasicrystals [6], and in alkali metals [9] have been performed.

3. Present Stage of our Diffusion Studies on Amorphous Si$_{26}$C$_{41}$N$_{33}$

3.1. Simulation of Silicon Self-Diffusion by $^{71}$Ge Diffusion

The diffusion of $^{71}$Ge in amorphous Si$_{26}$C$_{41}$N$_{33}$ has been studied by means of the radiotracer technique in combination with ion-beam sputtering for serial sectioning. The implantation of radioactive $^{71}$Ge ions with an energy of 30 keV was done at the mass separator of Bonn University. Fig. 2 shows the implantation profile together with a diffusion profile obtained after subsequent diffusion annealing for 4 h at 1200°C. The broadening of the implantation profile due to diffusion permits the calculation of the diffusion coefficient at the corresponding diffusion temperature. The Arrhenius diagram in Fig. 3 gives an overview of the $^{71}$Ge diffusivities measured as a function of the diffusion temperature in the as-produced state of amorphous Si$_{26}$C$_{41}$N$_{33}$ and after pre-annealing at various temperatures above the production temperature of 1050°C, respectively. It is seen that, irrespective of the thermal
Fig. 2. $^{71}$Ge profiles in amorphous $\text{Si}_{26}\text{C}_{41}\text{N}_{33}$ after implantation with an energy of 30 keV (filled circles) and after subsequent diffusion annealing for 4 h at 1200°C (empty triangles). The dashed and solid curves are a Gaussian distribution and an appropriate solution of the diffusion equation adjusted to the implantation and diffusion profiles, respectively.

pre-treatments of the specimens, the $^{71}$Ge diffusivity follows Arrhenius laws. Pre-annealing leads to a slight increase of the diffusion enthalpy from 4.65 eV in the as-produced state to about 5.5 eV after pre-annealing at 1350°C, but leaves the pre-exponential factor $D_0$ (≈ 0.2 m²/s) of the Arrhenius laws unchanged. Presumably these pre-annealing-induced changes are related to a decomposition of the material into amorphous $\text{Si}_3\text{N}_4$ and an amorphous C-rich phase, as found from X-ray- and neutron-scattering experiments [10].

3.2. Diffusion of $^{195}$Au

By implantation of the short-lived radioisotope $^{195}$Hg (half-life $t_{1/2} = 9.5$ h) with an energy of 60 keV at ISOLDE, the decay product $^{195}$Au ($t_{1/2} = 183$ d) has been introduced into amorphous $\text{Si}_{26}\text{C}_{41}\text{N}_{33}$ in order to study the diffusivity of Au. The diffusion profiles indicate that there are two separable contributions to the diffusion of this element. Correspondingly, Fig. 4 shows two Arrhenius lines with diffusion enthalpies of 2.7 eV and 3 eV, respectively. It is tempting to relate this behaviour to the diffusion of Au in the two different amorphous phases into which $\text{Si}_{26}\text{C}_{41}\text{N}_{33}$ starts to decompose even in the as-produced state [10].
In accordance with the experience well-established for crystalline solids, the lower activation enthalpies of the diffusion of Au in comparison to that of Ge may indicate that in amorphous Si$_{26}$C$_{41}$N$_{33}$ Au undergoes direct diffusion whereas Ge diffuses indirectly with the aid of intrinsic defects. This working hypothesis may either be confirmed or revised by further experiments.

4. Prompt In-Situ Diffusion Studies of the Short-Lived Radioisotopes $^{11}$C and $^{13}$N in Amorphous Si$_{26}$C$_{41}$N$_{33}$ after Implantation at ISOLDE

As already emphasized in Section 1, it is important to know the self-diffusivities of Si, C, and N in amorphous Si$_{26}$C$_{41}$N$_{33}$. These cannot be determined by the radiotracer technique in its conventional form, since there are no radioisotopes of these elements with suitable half-lives. In the case of Si diffusion this problem has been circumvented by simulating Si diffusion by that of $^{71}$Ge (Section 3.1).

Concerning C diffusion the use of the well-known isotope $^{14}$C would require dangerously high concentrations of this very long-lived radioisotope ($t_{1/2} = 5730$ a). Therefore, in a test experiment $^{11}$C ($t_{1/2} = 20.38$ min) has been implanted at ISOLDE and, within a few half-lives, the implantation profile and a diffusion profile after a 20 min anneal at 1050$^\circ$C have been determined.

![Arrhenius diagram of the diffusivities of $^{71}$Ge in amorphous Si$_{26}$C$_{41}$N$_{33}$ in the as-produced state (filled triangles) as well as after pre-annealing at 1200$^\circ$C (filled circles) or 1350$^\circ$C (filled squares).]
Fig. 4. Arrhenius diagram of the diffusivities of $^{195}\text{Au}$ in as-produced amorphous Si$_{26}$C$_{41}$N$_{33}$. The two Arrhenius lines are tentatively ascribed to different diffusivities in two coexisting amorphous phases.

measured (Fig 5). From the fact that both profiles are congruent, it is concluded that at 1050°C the diffusivity of carbon in amorphous Si$_{26}$C$_{41}$N$_{33}$ is unmeasurably small. Thus the question arises how the phase separation of amorphous Si$_{26}$C$_{41}$N$_{33}$ observed in scattering experiments [10] can take place. As a consequence, the performance of further $^{11}$C diffusion studies at different temperatures has a high priority and therefore is part of this proposal.

Measurements of the diffusion of N require similar efforts, since the available radioisotope $^{13}$N possesses an even shorter half-life ($t_{1/2} = 9.96$ min) than $^{11}$C. It is proposed to the ISC to perform such measurements, too. In addition, in a later stage of our investigations the diffusivities of both $^{11}$C and $^{13}$N in amorphous Si$_{2}$N$_{4}$ and amorphous carbon, the phases into which amorphous Si$_{26}$C$_{41}$N$_{33}$ decomposes, will be measured.

Obviously, diffusion studies with radioisotopes of extremely short half-lives (e.g., $^{11}$C and $^{13}$N), which in the past have been thought to be undoable, require a prompt high-speed in-situ sectioning of the specimens immediately after implantation and diffusion annealing. This can be done in the facility shown in Fig. 6, which has already been used in the $^{11}$C test experiments mentioned above. In such an experiment a 60 keV-$^{11}$C$^{16}$O$^+$ beam is led from the ISOLDE target onto the specimen for $^{11}$C implantation. For in-situ diffusion annealing, the specimen is heated by means of two halogen lamps through glass rods acting as light conductors. Finally, in-situ specimen sectioning is done by means of an Ar$^+$-ion-beam source at the unusually high sputtering rate of about 20 nm/min. The amount of sputtered-off specimen material that is collected on the foil segments is determined by a quartz resonator.
5. Experimental Requirements

By means of 1 GeV-proton bombardment of a CaO target, at ISOLDE two kinds of radioactive ions can be produced which are suitable for the scheduled experiments described in Section 4, namely $^{11}$C$^{16}$O$^+$ and $^{13}$N$^+$ for measuring the self-diffusion coefficients of C and N, respectively, in amorphous Si$_{26}$C$_{41}$N$_{33}$, amorphous Si$_3$N$_4$, or amorphous C.

It is intended that in a first series of experiments in the course of one year the diffusivities of $^{11}$C and $^{13}$N in the amorphous ceramics Si$_{26}$C$_{41}$N$_{33}$ are measured. This requires working at ISOLDE for two weeks, one week for doing the $^{11}$C experiments and one week for the $^{13}$N experiments. This does not mean at all that we shall use the ISOLDE beam for two full weeks, as will be explained in what follows.

Determination of the $^{11}$C diffusivity at a given temperature requires implantation of $^{11}$C$^{16}$O$^+$ ions at a rate of $1 \times 10^7$ ions/s for 40 min ($\approx$ 2 half-lives). The optimum implantation energy is 30 keV, but the standard energy of 60 keV would also be acceptable. Such an implantation will be followed by a 3-h period during which diffusion annealing, specimen sectioning, and measurements of specific radioactivity will be done. During these 3 h the beam will be available to other users. Hence, the determination of the diffusivity of $^{11}$C at one temperature requires half a day, i.e., within a one-week working period $^{11}$C diffusivities at 10 temperatures can be measured.

![Graph]

Fig. 5. $^{11}$C profiles in amorphous Si$_{26}$C$_{41}$N$_{33}$ after implantation (filled circles) and after subsequent diffusion annealing for 20 min at 1050°C (empty triangles). The solid curve is a Gaussian distribution adjusted to the implantation data.
Fig. 6. Facility for prompt in-situ diffusion measurements of short-lived radioisotopes after their implantation at ISOLDE.
For the determination of the $^{13}$N diffusivity at a given temperature, implantation of $^{13}$N$^+$ ions at a rate of $2.4 \times 10^4$ ions/s is required for 20 min ($\approx 2$ half-lives). Again such an implantation will be followed by a 3-h period during which the ISOLDE beam is available for other users. In total, the $^{13}$N diffusivity measurements will require about 10 implantations for about 20 min within one week.

In a second stage, diffusivity measurements of $^{11}$C and $^{13}$N in amorphous Si$_3$N$_4$ are scheduled. Again this will require ten 40 min-implantations of $^{11}$C$^{16}$O$^+$ within one week and ten 20 min-implantations of $^{13}$N$^+$ within a second week. The same is true for the final stage, in which the diffusivities of $^{11}$C and $^{13}$N in amorphous C shall be determined.

In none of these experiments the radioactivity of the specimens will exceed $4 \times 10^4$ Bq.

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References

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SUMMARY

A challenging research project at the Max-Planck-Institut für Metallforschung, Stuttgart, and Stuttgart University deals with the production of ceramics from polymeric precursors. An important step in this production route is a pyrolytic treatment at 1050°C, which leads to intermediate products, namely covalently bonded amorphous ceramics consisting of Si, C, N, and sometimes B, e.g., Si$_{26}$C$_{41}$N$_{33}$, which will be the prime subject in the investigations to be proposed. Annealing at temperatures above 1400°C ends up with the final product, a crystalline ceramics.

The chemical reactions and structural changes leading from the amorphous transitory state to the final crystalline ceramics are diffusion-controlled. Therefore, the understanding of self-diffusion and the knowledge of the self-diffusion coefficients of the components of amorphous Si$_{26}$C$_{41}$N$_{33}$ is of enormous technological importance. In addition, such investigations are also of great interest from a scientific point of view, since Si$_{26}$C$_{41}$N$_{33}$ will be the thermally most stable amorphous solid on which diffusion studies will have been performed. Hence, it is proposed to measure the self-diffusivities of C and N in amorphous Si$_{26}$C$_{41}$N$_{33}$ and, in a later stage, also in amorphous Si$_3$N$_4$ and amorphous C, which are the phases into which amorphous Si$_{26}$C$_{41}$N$_{33}$ decomposes.

Since the most reliable method for measuring diffusivities in solids is the radiotracer technique and since the only radioisotopes of C and N suitable for this are the very short-lived $^{13}$C ($t_{1/2} = 20.38$ min) and $^{13}$N ($t_{1/2} = 9.96$ min), these radiotracers have to be implanted into the specimens. This can be done at ISOLDE, where $^{13}$C and $^{13}$N can be produced as $^{13}$C $^{16}$O$^+$ and and $^{13}$N$^+$ by proton bombardment of a CaO target at yields of $1 \times 10^7$ and $2.4 \times 10^4$ ions/s, respectively. The optimum implantation durations resulting in the radioactivities required for diffusion studies are two half-lives. The implantations will be followed by prompt in-situ diffusion annealing, specimen sectioning by ion-beam sputtering, and sectionwise measuring of the specific radioactivities of the sputtered-off material. In a first series of experiments in which the diffusivities of $^{13}$C and $^{13}$N in amorphous Si$_{26}$C$_{41}$N$_{33}$ shall be measured, we should like to use ISOLDE for ten 40 min-implantations of $^{13}$C within a week and ten 20 min-implantations of $^{13}$N within another week. The optimum implantation energy would be 30 keV, although the standard energy of 60 keV is acceptable as well.