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An apparatus for \textit{in situ} spectroscopy of radiation damage of polymers by bombardment with high-energy heavy ions

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A new target station providing Fourier transform infrared (FT-IR) spectroscopy and residual gas analysis (RGA) for \textit{in situ} observation of ion-induced changes in polymers has been installed at the GSI Helmholtz Centre for Heavy Ion Research. The installations as well as first \textit{in situ} measurements at room temperature are presented here. A foil of polyimide Kapton HN\textsuperscript{®} was irradiated with 1.1 GeV Au ions. During irradiation several \textit{in situ} FT-IR spectra were recorded. Simultaneously outgassing degradation products were detected with the RGA. In the IR spectra nearly all bands decrease due to the degradation of the molecular structure. In the region from 3000 to 2700 cm\textsuperscript{−1} vibration bands of saturated hydrocarbons not reported in literature so far became visible. The outgassing experiments show a mixture of C\textsubscript{2}H\textsubscript{4}, CO, and N\textsubscript{2} as the main outgassing components of polyimide. The ability to combine both analytical methods and the opportunity to measure a whole fluence series within a single experiment show the efficiency of the new setup. © 2011 American Institute of Physics. [doi:10.1063/1.3571301]

I. INTRODUCTION

The most effective irradiation in terms of radiation damage takes place when material is being irradiated with heavy ions having high energies. A heavy ion loses its energy mainly by interaction with the electronic system of the target material. The relatively large linear energy transfer in the range of kiloelectronvolt per nanometer is sufficient to break any atomic bonds, and thus is very efficient for causing radiation damage.

Situations where materials are degraded by heavy ions can be found in space as well as in high-energy particle accelerators, where satellites, spacecrafts, or components of the accelerator are hit by heavy particles of very high energy.\textsuperscript{1} Knowledge of the degradation mechanism of the respective material is important for the lifetime of space devices and accelerator components. Radiation damage can be simulated with experiments using the Universal Linear Accelerator (UNILAC) at the GSI Helmholtz Centre for Heavy Ion Research in Darmstadt, Germany, which provides ion species from protons to uranium in the energy range from 1.4 to 11.4 MeV/\textmu{}t.

This work reports on a new \textit{in situ} setup to study ion-induced changes in polymers. These are known to degrade easily under the bombardment of swift heavy ions compared with metals or ceramics. The ion irradiation leads to the production of radicals and charged species that react with the organic system of the polymer.\textsuperscript{2, 3} These reactions result in chain scission, cross linking, creation of unsaturated hydrocarbons, carbonization as well as loss of volatile degradation products.\textsuperscript{4, 5} These effects result in distinct alterations to both the physical and chemical properties of the polymer within a cylindrical damage zone of a few nanometers called the latent ion track (core) surrounded by a region of slightly damaged material (halo).\textsuperscript{6} Such material modifications offer the production of mesopores,\textsuperscript{7–10} but significantly alter material properties such as electrical insulation ability and mechanical strength.\textsuperscript{11} Fourier transform infrared (FT-IR) spectroscopy and residual gas analysis (RGA) are common tools to investigate irradiation-induced modifications in polymers.\textsuperscript{12, 13}

In \textit{ex situ} experiments the material under examination needs to be irradiated and transferred to the lab for final characterization, with one sample for each irradiation parameter set. \textit{In situ} investigations have great advantages compared to common \textit{ex situ} investigations. Synthesized polymer foils are often of inhomogeneous thickness but can be measured quantitatively because of the fixed measurement position. Postdegradation effects due to the exposure to air can be suppressed. The ion-induced degradation can be followed precisely by measuring multiple spectra making experiments time and cost effective.

At the GSI recently three new target stations M1 to M3 have been installed at the so-called M-branch beamline, with M standing for materials research.\textsuperscript{14} One of these target stations, M3, offers simultaneous \textit{in situ} FT-IR spectroscopy and RGA to study the ion-induced degradation of polymers. In this paper the installed target station M3 as well as first results on Kapton HN\textsuperscript{®} type polyimide are described. Apart from aerospace applications, polyimide is important as cable...
insulation for the new SIS100/300 superconducting magnets of the Facility for Antiproton and Ion Research (FAIR) of the GSI. During the scheduled long-term operation of FAIR some accelerator components will be exposed to high radiation levels. When the material is hit by heavy ions, the tolerable radiation dose limit may be reached in a short time. The understanding of the degradation processes is important for future lifetime estimations and the planning of service intervals.

II. SETUP

The setup of target station M3 is shown in Fig. 1. At the beamline entry, the ions first pass an aperture consisting of a variable x-y-slit pair for ion beam shaping. Afterward, a secondary electron transmission monitor (SEETRAM), a Faraday cup, and a luminescence screen with a CCD camera for beam diagnostic are available. The SEETRAM is used for online ion flux monitoring during the irradiation and is calibrated using the Faraday cup (precision $\sim 10\%$–20\%). After the beam diagnostic unit a heater chamber allows heating experiments up to 1100 K to be conducted. The multipurpose diagnostic chamber (Fig. 2) found at the end of M3 contains a sample holder arrangement connected to the cooling finger of a closed cycle refrigerator. Temperatures down to 10 K can be obtained. The nearly free-standing sample holder unit can be moved 90 mm up and down and it can be rotated around $\pm 180^\circ$. For materials research investigations the chamber provides the FT-IR spectroscopy system and the RGA system.

For FT-IR spectroscopy a NICOLET 6700 FT-IR spectrometer of ThermoFisher Scientific is used. The spectrometer case providing the infrared (IR) source was placed outside the analysis chamber $\sim 45^\circ$ with respect to the ion beam normal (Figs. 2 and 3). The IR detection unit was separated from the casing of the spectrometer and installed outside the chamber at $+135^\circ$ with respect to the ion beam (Figs. 2 and 3). The infrared transparency is ensured by using two flanges including 4 mm thick ZnSe windows. In front of the first IR window sufficient space for a KRS-5 IR polarizer was left. It can be noted that even though the infrared beam has to pass through the KRS-5 IR polarizer, two ZnSe windows, the sample, and some air between the gaps of the IR source and the IR detector, IR spectra with very good signal intensity can still be obtained.

For residual gas analysis the Microvision Plus quadrupol mass spectrometer of MKS Instruments providing a mass range from 1 to 200 amu and a detection range from $6.7 \times 10^{-12}$ to $6.5 \times 10^{-4}$ mbar is used. The RGA is located $112.5^\circ$ in relation to the ion beam. Furthermore, the RGA is tilted $30^\circ$ downward. Electron ionization operates at an accelerating voltage of 70 V.

III. EXPERIMENTAL

A 12 $\mu$m thick foil of poly(pyrromellitimide) (Kapton HN®, DuPont de Nemours) was used in the first simultane-

![FIG. 1. Schematic layout of target station M3: Ions have to pass the aperture for ion beam shaping, a beam diagnostic unit providing a SEETRAM, a Faraday cup, a luminescence screen, and a heater chamber to reach the multipurpose diagnostic chamber.](image1)

![FIG. 2. (Color online) Schematic layout of the multipurpose chamber at target station M3. IR source and detection unit are placed outside of the chamber. The angle between IR radiation and ion beam normal is $-45^\circ$. The RGA is mounted near the IR detection unit and tilted down $30^\circ$. The sample holder can be moved up and down and is rotatable.](image2)
In situ FT-IR spectroscopy and outgassing experiments. As mentioned before, this polyimide has found a wide range of applications such as insulating material in components for extreme conditions (e.g., spacecrafts, aircrafts, accelerator magnets, etc.). Compared with other polymers, polyimide exhibits high resistance against ionizing radiation.

The polyimide sample (diameter 1 cm) was fixed on a sample holder and mounted into the multipurpose diagnostic chamber. For the experiments the irradiation chamber was evacuated to the $10^{-7}$ mbar range. Before starting the FT-IR measurements the sample was turned to an incident angle of $54 \pm 0.5^\circ$ for the IR radiation (corresponding to $+9 \pm 0.5^\circ$ of the ion beam) in order to ensure use of the Brewster’s angle. Using the infrared polarizer in combination with the sample in Brewster’s angle, unwanted undulations coming from interference of reflections within the sample were sufficiently suppressed.

The IR background spectrum in the wave number range from 4000 to 400 cm$^{-1}$ was measured through an empty sample position without ion irradiation. For all infrared spectra, four added scans were collected with a spectral resolution of 2 cm$^{-1}$. The time for one measurement using this setting is less than 2 min. Simultaneously, a background spectrum was measured by the RGA. The sample was then irradiated with a pulsed ion beam of 5.4 MeV/u $^{197}$Au ions at 5 Hz with a flux of $4 \times 10^8$ ions/cm$^2$s until a fluence of $5 \times 10^{10}$ ions/cm$^2$ was reached. The time for one pulse was 3.4 ms and the spot size of the ion beam was about 1.2 cm$^2$. An RGA spectrum of the outgassing molecule species was continuously recorded during irradiation. Out of this spectrum, after subtracting the RGA background spectrum of the chamber, the mass/charge ($m/z$) ratios, such as carbon C ($m/z = 12$), $C_2H_2$ ($m/z = 26$), and $C_2H_4/CO/N_2$ ($m/z = 28$), were selected to be monitored in the following step of irradiation. Thereafter, the sample was irradiated as described above up to a total fluence of about $1 \times 10^{12}$ ions/cm$^2$ using similar beam settings. During this second step of ion irradiation several FT-IR spectra were recorded.

Assuming cylindrical tracks having a radius of $\sim 3$ nm (given track radius for the ion-induced production of alkynes in polyimide from Ref. 20) the irradiated effective area of the sample is about 28% having 15% of overlapping track-area. A strong influence of double hits is, therefore, not expected.

**IV. EXPERIMENTAL RESULTS**

**A. Infrared spectroscopy**

Figure 4 shows the infrared spectra recorded before and after the irradiation (maximum fluence: $1 \times 10^{12}$ ions/cm$^2$). In the spectra the typical ion-induced degradation of polyimide becomes visible: nearly all IR bands decrease due to the degradation of the polymer structure. Also new peaks appear due to the creation of unsaturated hydrocarbons, –CN, –CC triple bonds, and oxidative degradation products.

**B. Residual gas analysis**

Figure 6 shows the residual gas spectra of polyimide. The diagrams indicate the background spectrum, the sample spectrum during irradiation, and their differential spectrum. Without the ion beam besides surface contaminations and background gases such as H$_2$O ($m/z = 18$), CO ($m/z = 28$), and CO$_2$ ($m/z = 44$), some signals from fragmented...
FIG. 5. IR spectra in the wave number range from 3000 to 2700 cm\(^{-1}\) of polyimide irradiated with different fluences. Here, the appearance of four new bands is shown. These bands could be identified as saturated carbon–hydrogen bonds and/or carboxylic acids of different degradation products.

hydrocarbons (\(m/z = 25–27\)) are detected coming from gas leakage and desorption from the surface of the chamber. With the start of ion irradiation these signals (i) increase and (ii) new signals are visible. The most pronounced difference in peak area is found for \(m/z = 28, 2, 26, \) and 12 in decreasing order. It is conclusive that a mixture consisting of \(C_2H_4, \) CO, and \(N_2\) molecules are the main degradation products which leave the polymer during the irradiation, as known from literature.\(^{13}\) Figure 7 shows the ion monitoring traces for carbon \(C (m/z = 12), \) \(C_2H_2 (m/z = 26),\) and \(C_2H_4/CO/N_2 (m/z = 28).\) Before the irradiation starts the partial pressure of all three molecules show a relatively low value. Starting the irradiation leads to a higher partial pressure for all chosen molecules caused by the degradation of the sample. At the onset of the irradiation all measured \(m/z\) values reach a plateau which presents a stationary state in the emission rate at the pumping efficiency of the turbomolecular pump. After beam stop the partial pressure returned to the value of the residual gas of the vacuum system.\(^{21}\)

C. Ion-induced degradation mechanism of polyimide

Numerous groups investigated the interaction between energetic heavy ions and polyimide type polymers. Despite the overall degradation of the polymer\(^{15}\) as well as ion induced carbonization\(^{22}\) the synthesis of degradation products such as cyanates and alkynes is found. Figure 8(a) shows a plausible degradation mechanism described in Refs. \(^{13}\) and \(^{23}\). A sufficient explanation on how the ion beam triggers the synthesis of –NCO and –CC triple bonds is found in the cleavage of the imide group which leads to the formation of CO, phenyl isocyanate, acetylene, and a biradical at the phenyl residue \([1 \text{ in Fig. 8(a)}].\) This radical furthermore reacts in different pathways forming CO, isomeric isocyanates as well as carbon clusters (reaction scheme (b) in Fig. 8).

In literature no mechanism describes the production of a nonvolatile carboxylic acid found in this study. In Fig. 8(c) we propose a reasonable synthesis path of a carboxylic acid not outgassing from the bulk polymer. Breaking of the C–N bond produces an imide radical. Hydrolysis of this radical possibly produces a carboxylic acid \([\text{Fig. 8(c)}].\) A similar reaction was proposed for the degradation mechanism of polyimide during pyrolysis.\(^{24}\)

An explanation for the formation of saturated hydrocarbons is found in analogy to the radiolysis of polytetrafluoroethylene (PTFE). In Ref. \(^{25}\) it is demonstrated that in the...
electron beam-induced radiolysis of PTFE a –CF₃ radical is formed which recombines with the backbone to a –CF₃ side group. In this way, it is possible to branch PTFE with –CF₃ side groups. A similar synthesis of –CH₃ side groups originating from the recombination of a –CH₃ radical with the polymer backbone seems reasonable. This mechanism is supported by the detected CH₄ (m/z = 16) as a minor outgassing product, but still needs verification by other methods, for example, nuclear magnetic resonance spectroscopy.

V. CONCLUSION

Highly energetic heavy ions with an energy transfer into material, beyond a certain limit, lead to material modification due to the radiation damage. In addition to the ion mass and their energy, the effects depend on the overall number of ions received by the material, i.e., the fluence. Damage is observable at very low fluences and may change its character with higher fluences. In order to be able to study the dependence of damage on ion beam parameters, a large number of experiments are required. Here, a new experimental setup of in situ analysis of polymers has been presented and its performance has successfully been proved. It facilitates to measure degradation of polymers, based on both the change of the polymer structure and the formation of small fragment molecules. In addition to the advantage that a whole fluence series can be observed with one sample only it turned out that new peaks of minor intensity can be distinguished from the measurement background.

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