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Articles

Determination of Degradation Constants of Energetic ^{7*}Li Ion in Liquid Media Using a Thin Boron Film on Silicon Wafer

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A novel method to determine degradation constants has been developed for energetic ^{7*}Li ions produced from the ^{10}B(n,α)^{7*}Li reaction, moving in liquid media. The energetic ^{7*}Li generated in a thin boron film on silicon wafer plunged into a liquid sample in which the wafer was immersed. The degradation constants were determined by analyzing the Doppler-broadened lineshapes of prompt γ-ray at 478 keV emitted from ^{7*}Li. For comparison, degradation constants were also measured for solutions of boron compounds. Values obtained by the two methods gave fair agreement.

Introduction

Stopping powers of materials for charged particles with sub-MeV order of kinetic energy have been obtaining growing interest because of the expanding needs in material science, radiation therapy, analytical use etc., where the depth profiles of the implanted particles in substrates have critical importance. They have been usually determined by measuring energy loss of energetic ions through passage of thin foils. However, it is difficult to adopt such a method for sub-MeV particles because their short stopping range requires very thin foils which are available only for limited materials. The method using stacked thin foils cannot be applicable to gas and liquid materials. Among the methods of measuring stopping powers of relatively low energy ions, the unique lineshape analysis of the 478 keV prompt γ-ray from ^{7*}Li produced via the ^{10}B(n,α)^{7*}Li reaction has been applied not only to solids but also to liquids and gases. Usually small amount of boron mixed or doped in the sample of interest act as a ^{7*}Li source. An energetic ^{7*}Li with an initial kinetic energy of 840 keV decays to ^{7}Li with a lifetime of 1.05×10^{-13} s, emitting the γ-ray. Due to coincidental matching of the lifetime and the slowing-down time, the ^{7*}Li emits the γ-ray in flight in medium, resulting in Doppler broadening of the spectral lineshape of the γ-ray. The degree of broadening depends on velocity degradation of ^{7*}Li in the medium, that is, on the elemental composition and atomic density of the materials.

Previously, we have measured the Doppler broadened lineshapes of the prompt γ-rays of 478 keV in various samples containing boron using neutron beam guides of JRR-3M at Japan Atomic Energy Research Institute (JAERI). The "Degradation constant" *D* was introduced and defined as the reciprocal of the time constant of the degradation in media.[1, 2] The stopping power and degradation constant are the values evaluated for an identical phenomenon from different viewpoints; the former is one from a viewpoint of the materials, while the latter from the moving charged particles.

Kreutz et al.[3] employed the "solution method" and used boric acid and its derivatives as boron sources for liquid samples. Although boric acid is considerably stable, it dissolves to limited range of organic compounds. Boric esters were also used for organic compounds, but they are not stable to humidity and decompose upon exposure to air. The method is not applicable to the substances which do not dissolve any boron compounds with considerable amount. Such limitation has prevented the measurement of stopping powers of wide class of compounds by this method.

Our recent works[4,5] proved that the lineshapes of the Doppler broadened γ-ray spectra of a thin boron film are asymmetrical. This phenomenon was successfully explained by assuming that energetic ^{7*}Li ions are ejected from the thin boron film. In the present study, we proposed a novel "thin film" method using a thin boron film deposited on a silicon wafer as a ^{7*}Li source. By immersing the wafer in sample liquids we measured the Doppler broadened γ-ray spectra from the ^{7*}Li ions ejected from the thin boron layer to the target liquid.

Experimental

Sample Preparations. Organic solvents were used of a research grade commercially available from Wako Pure Chemical Co. For the solution method borane dimethylamine, $BH_3NH(CH_3)_2$, abbreviated as BDA, from Kanto Chemical Co., Inc. was dissolved in pure liquid media with a weight concentration of 0.2 %. BDA is chemically stable and sufficiently soluble in various polar and non-polar solvents. About 0.5 ml of the sample solution was placed in a quartz tube (5 mmϕ × 35 mm height) with a rubber cap. For the thin film method, a mirror-polished silicon wafer of approximately 3 × 5 × 0.05 cm^3 was used as a substrate. A thin boron layer of about 50 nm was formed on the wafer using the Ar ion sputtering method. The wafer was cut into chips of approximately 1 × 1 cm^2.

Prompt γ-ray Measurements. At the neutron beam guide of JRR-3M at JAERI a solution sample in quartz tube was irradiated with thermal or cold neutrons, the flux of which was 2.4 × 10^7 and 1.1 × 10^8 cm^{-2}s^{-1}, respectively. A wafer immersed in a liquid sample of about 1 ml in a polyethylene tube was irra-

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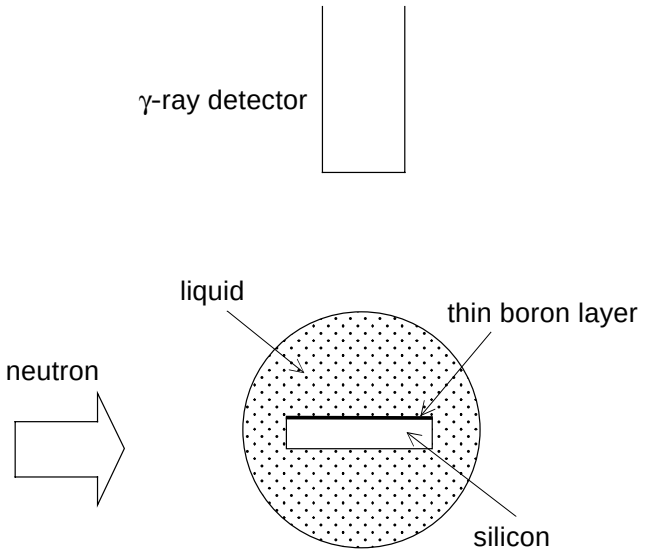

Figure 1. Conceptual arrangement for the measurement using a B/Si wafer. The thickness of boron layer was 50 nm and the wafer size is 1×1 cm². The distance between the wafer and the detector was 30 cm. The B/Si wafer was immersed in a liquid sample and the boron layer was set perpendicular to the measurement axis.

diated in the same conditions as described above. The conceptual measurement arrangement is shown in Figure 1, where the thin boron layer was set to be perpendicular to the measurement axis and faced to the detector. The measurements were performed using the prompt γ-ray analyzing system installed at the neutron beam guide by Yonezawa et al.[6, 7] The γ-ray spectrometry system consisted of a high purity Ge detector, bismuth germanate shielding detectors, and pulse height analyzers controlled by a personal computer.

Lineshape Analysis. In our previous works, a parameter called "degradation constant" *D* was introduced. The velocity of ^{7*}Li at time *t*, *v(t)*, is expressed in its lifetime in the following;

$$v(t) = v_o \exp(-Dt), \quad (1)$$

where v_0 is the initial velocity of ^{7*}Li , 4.8×10^8 cm s^{-1}. *D* values are characteristic property of the media in which the energetic ^{7*}Li ion loses its kinetic energy. The lineshapes of the Doppler broadened spectra depend greatly on the degradation constant *D*. Recently we proposed a formula describing the lineshape *g(E)* containing *D* as follows;[8]

$$g(E) = \frac{cN_0}{2E_0 v_0} \frac{\lambda}{\lambda - D} \left[1 - \left(\frac{c\,|E - E_0|}{E_0 v_0}\right)^{\frac{\lambda - D}{D}}\right], \quad E_0(1 - v_0/c) \le E \le E_0(1 + v_0/c). \quad (2)$$

In the above equation, *c* is the velocity of the light, N_0 the number of ^{7*}Li at $t = 0$, E_0 the center energy of the prompt γ-ray emitted from ^{7*}Li (= 478 keV), and λ the decay constant of ^{7*}Li (= 9.49×10^{12}s^{-1}). An actual spectral lineshape is measured by convoluting the eq 2 with an instrumental response function usually assumed to be Gaussian. Therefore, in order to evaluate a *D* value, we fitted the combination of the eq 2 and a background function to data points of the prompt γ-ray spectrum.

Results and Discussion

The measured prompt γ-ray spectra at 478 keV of ^{7*}Li for BF_3 gas (900 torr), methanol solution of BDA, and glycerin solution of BDA are shown in Figure 2. The spectral lineshapes of 478 keV γ-ray for air/B/Si, methanol/B/Si, and glycerin/B/Si are shown in Figure 3. It is expected that a γ-ray emitted from a ^{7*}Li ion recoiling forward to media should

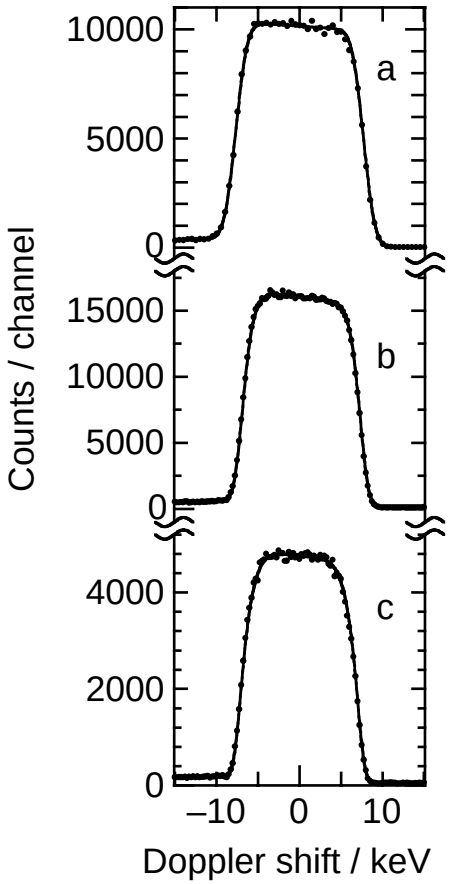

Figure 2. Spectral lineshapes of prompt γ-ray of 478 keV of ^{7*}Li measured for BF_3 (900 torr) (a), methanol solution of BDA with 0.2 wt% (b), and glycerin solution of BDA with 0.2 wt% (c). The abscissa indicates the Doppler shift from 478 keV.

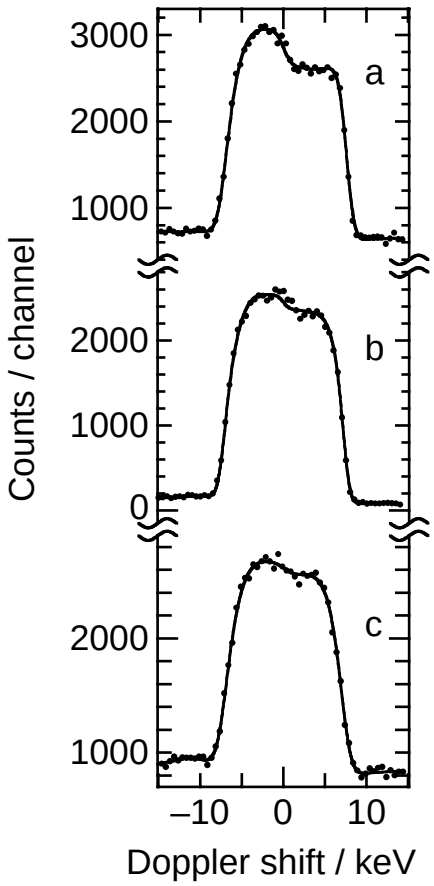

Figure 3. Spectral lineshapes of prompt γ-ray of 478 keV of ^{7*}Li measured for air/B/Si (a), methanol/B/Si (b), and glycerin/B/Si (c). The abscissa indicates the Doppler shift from 478 keV.

make a positive Doppler energy shift, while that recoiling backward to silicon substrate should shift its energy to negative. Thus, the measured spectra were analyzed as a superposition of the media and silicon for the positive and negative Doppler shift, respectively. The estimated Degradation constants *D* for air and liquid samples are summarized in Table 1.

The *D* values for BF_3 gas and air/B/Si were estimated from the lineshapes to be very small, nearly zero within the experimental error, indicating that no actual velocity degradation occurred in BF_3 gas of 900 torr and air at about 1 atm during the lifetime of ^{7*}Li. This finding also implies that the boron layer of the B/Si wafer targets prepared in the present work was actually thin enough compared with the range of ^{7*}Li that we can use the B/Si wafers as the source of energetic ^{7*}Li implanting to sample media for our purpose. It might be considered that ^{7*}Li ions traversing long in boron layer could affect the lineshape and lead to erroneous *D* values. But those ions have originally small velocity component along the measurement axis and should result in little Doppler shift whether they experience any degradation or not.

Comparing the *D* values for methanol, ethyleneglycol, and glycerin by the two methods listed in Table 1, we can conclude that both the methods gave same values in those organic liquids. This clearly shows that our novel method using a B/Si wafer to determine degradation constants is effectively applicable.

TABLE 1: Degradation Constants ($10^{12}s^{-1}$). *D*; Obtained in the Present Work, D_{LSS}; Calculated According to the LSS Theory and the Bragg Rule

	$D / 10^{12}s^{-1}$		$D_{LSS} / 10^{12}s^{-1}$
	"Solution method"	"Thin film method"	
BF_3 gas (900torr)	0.04 (1)		0.003
Air (1atm)		0.02 (15)	0.001
Methanol	0.96 (2)	1.08 (6)	1.13
Ethyleneglycol	1.24 (1)	1.28 (2)	1.46
Glycerin	1.38 (2)	1.34 (2)	1.63

The measurements for BF_3 gas (Thin film method) and air (Solution method) were not carried out since they are impossible to be done in principle.
D values contain the (error) in the last one or two decimal place(s) given in brackets. The errors were estimated from fitting results.

On the other hand, we calculated the degradation constants using the Lindhard-Scharff-Schiott (LSS) theory[9] and the Bragg rule,[10] where the simple additivity of stopping power for each constituent atom was postulated, neglecting any effect of chemical bonding. The details of calculation procedures are referred to our previous papers.[1, 2] The *D* values from the LSS theory (D_{LSS}) are also listed for BF_3 (900 torr), air (1 atm), liquid methanol, liquid ethyleneglycol, and liquid glycerin in Table 1. It was revealed that the *D* values experimentally obtained for methanol, ethyleneglycol, and glycerin are substantially lower than the respective D_{LSS} values. The difference might be due to some chemical effect on the degradation processes or stopping powers, which should be very interesting. It is anticipated that there could exist chemical-bond effects since the velocity range (5 to 2×10^6 m s^{-1}) of ^{7*}Li with its lifetime overlaps with those of the electrons participating in chemical bonds in medium, leading to the longer interaction time and consequently the more extent of chemical effect.[11] However, we have not yet offered possible concrete explanation on such chemical effects. Further research is necessary to take a clue for making clear the problems.

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