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Depth profiling of hydrogen under an atmospheric pressure

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ABSTRACT

Nuclear reaction analysis of hydrogen with a use of the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ reaction was performed under a atmospheric condition. A 100 nm-thick silicon nitride membrane coated with gold of 10 nm was used for the extraction of the ^{15}N beam into the sample chamber filled with gas molecules. Hydrogen contained in a Y film with a thickness of 80 nm was detected in N_2 of 10^5 Pa. This nuclear reaction analysis (NRA) setup was also applied to H_2 gas, and the yield curve revealed a plateau feature. The plateau level was, furthermore, found to be constant independent of the H_2 pressure. We show that this plateau intensity can be used to obtain the detection efficiency of a NRA setup.

1. Introduction

Interaction of hydrogen with solids is of technological importance as well as scientific interest in view of potential of hydrogen as a future clean energy source. Typical examples are hydrogen storage in metals and complex compounds, electrolytes for fuel cells, and an undesired phenomenon of hydrogen embrittlement. In these phenomena, hydrogen interacts with solid surfaces followed by absorption into bulk, or absorbed hydrogen migrates to the surface and is released from the surface. In any cases, behavior of hydrogen at material surfaces and in solids is particularly important, which is a hot topic in recent years [1,2].

A difficulty for the study of hydrogen near the surfaces of solids is that hydrogen is visible to limited experimental techniques, because of the small scattering factor and limited availability of electron spectroscopic techniques. High-energy ion beams offer a way to detect hydrogen. Two powerful methods to quantify hydrogen in solids in a non-destructive manner are nuclear reaction analysis (NRA) and elastic recoil detection (ERDA) with high-energy ion beams [3,4]. Both techniques are usually performed in a high vacuum condition.

In a typical hydrogen-absorbing material of Pd, the bulk phase diagram shows that two phases of hydrogen solution and hydride exist, and that the transition between the two phases occurs at room temperature and a hydrogen pressure of $\approx 10^3$ Pa [1,5,6]. In a fuel cell, on the other hand, hydrogen reacts with other molecules at the surface of catalysts in ambient conditions.

In order to examine the fundamental processes such as absorption, desorption, diffusion and reaction of hydrogen on and in materials and related phase transition of the systems, in situ measurements of hydrogen in gas atmosphere is strongly required. To achieve this, we have developed an NRA setup by using a glass capillary for differential pumping between the ion beam line and sample chamber [7]. By using the $^{1}H(^{15}N,\alpha\gamma)^{12}C$ nuclear reaction with this setup, hydrogen depth profiling with a depth resolution of $\approx$10 nm and a lateral resolution of $\approx$25 μm was successfully performed up to a pressure of 10 mbar [7]. Nevertheless, a serious increase of the background signal hindered the NRA measurement at a gas pressure of higher than 100 mbar [8]. High-energy ERDA has been applied to depth profiling of hydrogen in Ti hydride [9] and hydrogen absorption by Pd [10] under atmospheric conditions, where a depth resolution of 0.74 μm was achieved near the surfaces. As an alternative way to study hydrogen absorption by Pd, hydrogen concentration was probed at the back side of a Pd foil by conventional ERDA [11]. In the present paper, we report development of atmospheric NRA by using a silicon nitride membrane for the beam extraction, where the membrane separates the

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vacuum of the beam line and the gaseous condition of the sample chamber. We demonstrate hydrogen detection with the NRA setup in N_2 of 10^5 Pa. We also report the results measured for H_2 gas showing a plateau in the NRA yield curve. We discuss that the gas signal can be used to evaluate the detection efficiency of the NRA setup.

2. Experimental

The experiments were performed at the 1C beam line of the Van de Graaff tandem accelerator in Micro-Analysis Laboratory of the University of Tokyo. The nuclear reaction used in the present work is $^1H(^{15}N,\alpha\gamma)^{12}C$. This reaction has a narrow resonance of 1.8 keV at a ^{15}N energy of 6.385 MeV, which allows for high-resolution depth profiling [3,4]. A $C^{15}N^-$ beam was generated by a Cs-sputter type ion source with a $Ti^{15}N + C$ solid cathode, and a ^{15}N beam was accelerated to an energy of 6.4–9 MeV. After energy analysis with a sector-type double-focused magnetic analyzer (momentum dispersion: 5080 mm) and focusing with two quadrupole magnetic lenses [12,13], the typical size and current of the ^{15}N beam at the target were 200 μm in diameter and 20 nA, respectively.

A SiN membrane grown by low-pressure chemical vapour deposition with a size of 1×1 mm^2 and a thickness of 100 nm (Silson Ltd. UK) was used for beam extraction into an ambient condition, which is schematically shown in Fig. 1(a). The thin SiN membrane is suspended by a 0.2 mm-thick Si frame, which is attached to a stainless steel flange with vacuum glue. With a beam dose, the SiN membrane suffers from degradation eventually resulting in a gas leak and breakage. In order to enhance the mechanical durability against the incident ion beam, the SiN membrane was coated with 10 nm-thick Au. With this membrane, the sample chamber can be filled with a gas of up to 2×10^5 Pa, and the NRA measurement can be performed with a beam dose of more than 300 μC. It is noted that thermal radiation due to sample heating at >700 K causes a severe damage on the SiN membrane leading to immediate breakage upon beam irradiation. When the ^{15}N beam was misaligned with respect to the SiN membrane, an appreciable shift of the yield curve to a higher energy was observed probably because of sputtering and deposition of Si atoms of the frame onto SiN. After a careful alignment of the beam size and position, no significant energy shift was observed up to a beam dose of ca. 10 μC. After a prolonged measurement, however, a slight shift of the yield curve to a higher energy was occasionally recognized even with a careful beam alignment probably due to C deposition onto SiN during beam irradiation. All data presented here were acquired within a low beam dose where such beam effects were neglected.

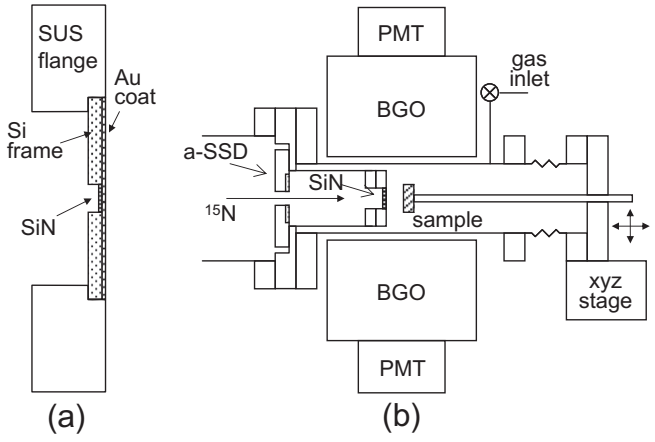

Fig. 1. Schematic of the experimental setup. (a) Schematic drawing of the SiN membrane used in the present study. (b) Schematic of the sample compartment and detector geometry.

Fig. 1(b) shows a schematic of the experimental setup around the sample. The beam coming from the vacuum side irradiates the sample through the SiN membrane, which separates the vacuum from the gas atmosphere of the sample chamber. While the upstream chamber is kept at a vacuum of 10^{-6} Pa, the downstream chamber can be filled with gases of up to 2×10^5 Pa. An annular SSD with a hole of 5 mm in diameter mounted 300 mm from the sample detects the backscattered ions from the Au film on SiN as well as from the sample. The distance between the SiN and the sample can be precisely changed from 0.1 to 20 mm with a linear stage controlled by a stepping motor. For the beam positioning, a movable mirror is set between the membrane and sample so that the sample surface can be observed with an optical microscope from the top of the chamber, and the sample position is precisely adjusted with respect to the beam with a xyz stage.

As shown in Fig. 1(b), two 4"-BGO scintillators mounted 30 mm from the sample outside the vacuum are used for γ-ray detection. The yield of γ-rays at 4.4 MeV due to the nuclear reaction is normalized to the Rutherford backscattering spectroscopy (RBS) signal from the gold layer on the SiN membrane, which is proportional to the ^{15}N beam current. The accelerator setup, i.e. the beam energy and lens/deflector parameters, and data acquisition, i.e. γ-ray detection, RBS measurement, beam current reading and sample positioning, are computer-controlled by a Labview-based software, which enables us to perform automatic beam-energy scan and NRA measurements.

The sample used in the present experiment is a Y thin film (about 80 nm) covered by 10 nm-thick Pd deposited on a glass substrate. This sample was exposed to a H_2 gas of 10^5 Pa prior to setting on the sample holder for NRA. The Y film was hydrogenated up to a H/Y ratio of 2–3. After evacuating the sample chamber, either N_2 or H_2 gas was introduced into the chamber up to a desired pressure as measured by a capacitance vacuum gauge.

3. Results and discussion

Fig. 2 shows the γ-ray yield curves measured for the hydrogenated Y film in N_2 gas of various pressures from 0 to 10^5 Pa. The γ-ray yield is measured as a function of the ^{15}N energy, and the yield is converted to the hydrogen concentration in the H/Y atomic ratio using the detection efficiency obtained by the following procedure described below. Fig. 2(a) is the yield curve taken in

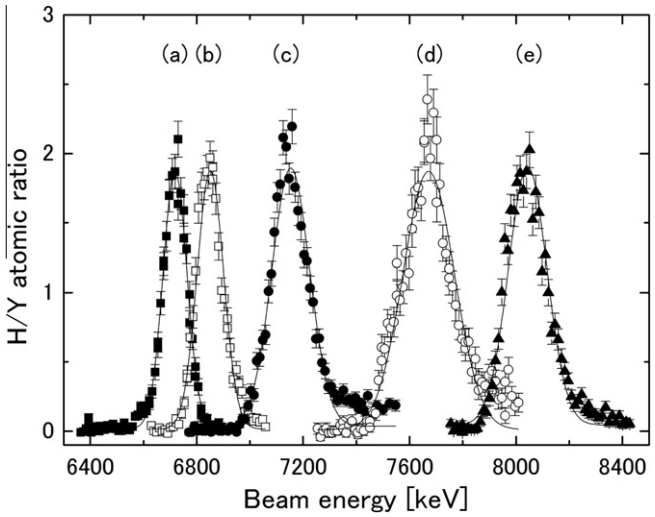

Fig. 2. NRA yield curves measured for a hydrogenated Y film (80 nm) deposited on a glass plate in N_2 gas of various pressures of (a) 0, (b) 1×10^4, (c) 3×10^4, (d) 7×10^4, and (e) 1×10^5 Pa.