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IN SITU MEV ION BEAM ANALYSIS OF CERAMIC SURFACES
MODIFIED BY 100-400 KEV ION IRRADIATION

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***In situ* MeV ion beam analysis of ceramic surfaces**

modified by 100-400 keV ion irradiation*

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Abstract

This paper describes use of the *in situ* ion beam analysis facility developed at Los Alamos National Laboratory for the study of irradiation effects in ceramic materials. In this facility, an analytical beamline of 3 MV tandem accelerator and an irradiation beamline of 200 kV ion implanter are connected at 60° to a common target chamber. This facility provides a fast, efficient, and quantitative measurement tool to monitor changes of composition and crystallinity of materials irradiated by 100-400 keV ions through sequential measurement of backscattering events of MeV ions combined with ion channeling techniques. We will describe the details of the *in situ* ion beam analysis and ion irradiation and discuss some of the important issues and their solutions associated with the *in situ* experiment. These issues include (1) the selection of axial ion channeling direction for the measurement of radiation damage; (2) surface charging and charge collection for data acquisition; (3) surface sputtering during ion irradiation; (4) the effects of MeV analytical beam on the materials; and (5) the sample heating effect on ion beam analysis.

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1. Introduction

A facility for the *in situ* ion beam analysis for research on materials surface modification has been recently developed at the Ion Beam Materials Laboratory (IBML) at Los Alamos National Laboratory (LANL) [1]. The detailed description of ion beam facilities at the IBML has been published elsewhere [2]. In the newly developed *in situ* facility, a 45° left beamline (analytical beamline) from a 3 MV tandem accelerator is joined by a second beamline (irradiation beamline) from a 200 kV ion implanter in a surface modification chamber (*in situ* chamber), as shown in Fig. 1. The analytical beamline is used for ion beam analysis of the materials, in particular for Rutherford backscattering spectrometry (RBS) measurement. The irradiation beamline is for ion irradiation of the materials. The angle between two beamlines on their co-plane is 60°. This facility provide a fast, efficient, and quantitative tool to monitor changes of stoichiometry and crystallinity of materials, irradiated by a 100-400 keV ion beam, using sequential RBS measurements of a MeV He ion beam. We used the *in situ* facility to study the kinetics of ion-beam-induced densification of sol-gel zirconia (ZrO_2) thin films [1,3] and radiation damage in several ceramic single crystals, e.g., MgAl_2O_4 [1,4], MgTiO_3 [5], and 6H-SiC [6] at different temperatures. In this paper, we will describe the basic aspects of *in situ* experiment in detail. Some of important issues associated with the *in situ* experiment will be discussed. These issues include (1) the selection of axial ion channeling direction for the measurement of radiation damage; (2) surface charging and charge collection for data acquisition; (3) surface sputtering during ion irradiation; (4) the effects of MeV analytical beam on the materials; and (5) the sample heating effect on ion beam analysis.

2. Sample installation

The samples used for ion irradiation study had a typical dimension of 1-3 cm width and 0.5 mm thickness. The samples were glued to a sample holder, made of pure copper, with silver paint to improve thermal conduction and reduce sample surface charging. The sample holder, with a dimension of 3.5 cm diameter and 2.5 mm thickness, was mechanically clamped onto a heating stage, which was seated on a multi-axis goniometer (Fig. 1). A disk-shaped resistive heater, made of hexagonal boron nitride and graphite composite, was permanently installed inside the heating unit. The heater allowed fast heating of the small sample holder and the sample up to 500°C

within 30 minutes. The sample could also be cooled to -100°C using liquid nitrogen conduction cooling. The edge of the sample holder was connected with a liquid nitrogen reservoir through a 3.5 mm diameter, 18 cm long pure copper braid. The reservoir, with a volume capacity of 64 cm^3 , was extended outside the chamber through an isolation vacuum feedthrough. Less than one hour was required to cool the sample stage from room temperature to -100°C . The temperature on the sample was monitored by a thermocouple attached to the edge of the sample holder, opposite to the cooling braid. The typical power load of an ion beam on the sample was 0.2 W or less during ion irradiation and ion beam analysis (400 kV, 0.5 μA and 2 MV, 100 nA). The temperature rise on the sample due to the beam heating was less than 5°C . Typical vacuum in the chamber was 2×10^{-7} torr.

3. Ion beam analysis and ion irradiation

For radiation effects study, RBS in conjunction with ion channeling techniques was employed to detect radiation damage in single crystal samples. The sample, mounted on the sample stage, was first aligned with one of its crystallographic axes along the 2 MeV He^+ ion beam from the tandem accelerator. The selection of axial ion channeling directions for radiation detection will be discussed in the next section. The size of the analytical beam was 2 mm diameter on the sample surface. Two gold-silicon surface barrier detectors (Fig. 1) were installed in the target chamber to detect backscattered He particles at scattering angles of 165° and 120° , respectively. The channeling alignment was performed by both sample tilt and rotation motion through a computer-controlled goniometer. The accuracy of the angular motion was better than 0.1° . For alignment, the rotation axis of the sample stage was co-planar with the He ion beam to avoid the motion of the analytical beam spot on the sample surface. The second step, after alignment, was to bring the sample to a temperature at which the ion irradiation was to be conducted. It was confirmed that the heating or cooling caused no measurable changes in the sample orientation. Then a channeling spectrum was taken on the sample prior to irradiation. The sample was irradiated to an incremental dose with the 100-400 keV ion beam from the ion implanter and subsequently analyzed with the 2 MeV He ion beam. The irradiation beam spot on the sample was 6 mm in diameter. The analytical beam was co-centered with the irradiation beam to ensure the detection of the radiation-damaged area on the sample. During ion irradiation, a

shutter blocked the detectors to prevent backscattered heavy particles from hitting the detectors. The irradiation experiment was carried on until the lattice disorder in the irradiated sample reached a certain saturation level such as amorphization. For samples with a large enough size, it was convenient to restart a similar irradiation experiment at a different temperature without breaking the vacuum. The sample could be translated vertically up to ± 2 cm through manual control (see Fig. 1) to set an unirradiated area exposure to the ion beams. No further realignment was required since the vertical motion introduced no measurable changes in the sample orientation.

For the ion beam densification experiment, the samples with sol-gel zirconia films coated on Si wafers were oriented directly at 60° with respect to the analytical beam and with normal incident to the irradiation beam [3].

4. Selection of axial channeling directions

To maintain equivalent experimental conditions throughout the radiation experiment, we always avoided changing the sample orientation once it was aligned. A key step was to choose a fixed axial channeling orientation of the sample for the detection of radiation damage, which compromised the incident geometry for both analysis and irradiation. Criteria for selecting an axial ion channeling direction included (1) minimizing the incident angle for the irradiation beam and (2) achieving the backscattering yield as low as possible. Small incident angle is preferable to glancing incident angle for the irradiation in order to minimize surface sputtering of the irradiated sample, which will be discussed in Section 6. Physically, there was always a 60° angle between two beamlines. We intended not to choose the major axial channeling direction close to the sample normal to avoid a 60° glancing incident for the irradiation. A specific channeling direction, with a relatively low backscattering yield, had to be selected among many crystallographic directions that were away from the sample normal. The channeling direction with a low minimum yield provided a high sensitivity to detect radiation damage in the single crystal sample. In reality, the optimum channeling axis was chosen based upon the structure and the orientation of the single-crystalline specimen. For cubic MgAl_2O_4 spinel with $\langle 100 \rangle$ orientation, the $\langle 110 \rangle$ axial channeling direction was chosen. The minimum yield along the $\langle 110 \rangle$ axis (3%) was even a little bit lower than that along the $\langle 100 \rangle$ axis (4%). The use of $\langle 110 \rangle$ axis for ion channeling

measurement maintained 45° and 15° incident angles of the analytical beam and the irradiation beam, respectively. For hexagonal structures such as 6H-SiC and MgTiO_3 , it is known that along a c-cut direction, i.e., $\langle 0001 \rangle$ axis, the lowest minimum yield is achieved (2%). On these materials with the c-cut orientation, however, we had to choose an axial channeling direction among crystallographic axes with relatively high Miller indices. For c-cut 6H-SiC crystal, the $\langle 1012 \rangle$ axis was selected, which has a 35.3° angle with respect to the c-axis. For c-cut MgTiO_3 crystal, the $\langle 1014 \rangle$ axis was used (a 35° angle to the c-axis). The minimum yields along these chosen directions were higher (7%) compared to the c-axis, as shown in Fig. 2, but they were still relatively lower compared to other adjacent channeling directions.

5. Surface charging and charge collection

The ceramic oxides we studied, such as MgAl_2O_4 and MgTiO_3 , were good electrical insulators. Sample surface charging due to ion charge accumulation by analytical and irradiation beams always existed and caused some problems. The surface charging interfered with charge collection to determine the delivered dose from analytical and irradiation beams. The constant charging and subsequent arcing could also severely distort the backscattering spectrum due to variation of the retarding potential (a few keV) on the sample surface. We developed several solutions to these problems. A four-corner Faraday-cup apparatus, used mostly for implantation processes in the semiconductor industry, was installed in the irradiation beamline near the *in situ* chamber (see Fig. 1). The irradiation beam was uniformly rastered across the entire area of the four-corner-cup during irradiation and only a small portion of the beam through a central aperture (6 mm diameter) was delivered onto the sample surface. The irradiation dose was determined by the charge collection from the four-corner-cup connected with a dose processor. The sample stage, which was isolated from electrical ground, was always biased at 300 V and connected with a current integrator for charge collection of the analytical beam during the *in situ* experiment. The bias was necessary to suppress secondary electron emission. Extra silver paint decorated along the edge of small samples (4 mm) could effectively reduce surface charging. The surface charging problems could be effectively solved if the insulating sample surface was coated with a thin layer (1-3 nm thick) of conducting material, such as a metallic film or an amorphous carbon film. The selection of heavy metals or carbon for surface coating could avoid the interference of the RBS

spectrum from the substrate with that from the thin film. Noble metals such as platinum and gold do not wet oxide surfaces, and therefore the thin coating does not form a continuous layer. We noted that iridium readily wets oxide surfaces, forming a conductive iridium oxide layer. Iridium coating effectively minimized charging effects on oxide ceramics.

6. Surface sputtering issues

The 100-400 keV irradiation beam not only introduced lattice disorder in the irradiated surface region (100-200 nm thick), but also caused surface sputtering (surface erosion). The surface sputtering became severe for heavy ion species such as Kr and Xe with a glancing incident geometry. The metallic coating on the oxide surface could be more readily sputtered off than the oxide surface due to the lower surface binding energy of metals. Fig. 3 shows channeling spectra of 2 MeV He ions from a (100) MgAl_2O_4 spinel sample, coated with an 1 nm gold thin film, before and after 370 keV Xe^{2+} ion irradiation at -50°C to a dose of $2 \times 10^{15} \text{ Xe/cm}^2$. The Xe ions were incident at 15° with respect to the sample normal. It is obvious, from the gold signal in the spectra, that the gold coating was almost completely removed by $2 \times 10^{15} \text{ Xe/cm}^2$, long before the spinel surface transformed into an amorphous phase at $2 \times 10^{16} \text{ Xe/cm}^2$ (data not shown). The removal of metallic film coating by sputtering could cause surface charging problems for analysis. However, most often surface charging became less severe after the sample had experienced a certain amount of irradiation dose. This was due to ion-bombardment induced carbon deposition from the vacuum chamber. The carbon deposition caused by the analytical beam will be discussed in the next section. The surface sputtering did not interfere with the kinetic study of radiation damage in the depth well below the surface (100-200 nm) since sputtering at most removed a 10 nm surface layer.

7. The effects of analytical beam on the materials

Ion irradiation and ion beam analysis were performed on the same sample area throughout each *in situ* experiment. To achieve good statistics for the backscattering spectrum and a good kinetic curve, each spectrum was taken with a fixed charge of 10-20 μC and twenty spectra were routinely collected on the same sample spot. The total charge of He^+ ions deposited in a sample area of 2 mm diameter was 200-400 μC , corresponding to doses of $(4-8) \times 10^{16} \text{ He/cm}^2$. These He

ions stopped in the target materials at a depth greater than 4 μm , which was beyond the regions of interest (100-200 nm) in our radiation damage studies. Furthermore, most of ceramics we studied were relatively radiation resistant in comparison to semiconductor materials such as Si and Ge. Therefore, a high dose irradiation with a MeV He ion beam introduced no observable radiation damage and chemical effects in the near surface region. Fig. 4 shows channeling spectra of 2 MeV He ions taken from a 6H-SiC crystal along the $\langle 0001 \rangle$ axis, irradiated with the same analytical beam to 40 and 400 μC . No difference in the dechanneling yield is observed over the entire displayed region (1 μm) except an increase in the area under the carbon surface peak. The increase in the carbon surface peak cannot be due to surface damage induced by the He ion beam since no corresponding increase in the silicon surface peak is observed in Fig. 4. Therefore, the increase in the carbon surface peak was caused only by ion-beam-induced carbon deposition from the vacuum.

For materials exhibiting sensitivity to ion irradiation, e.g., sol-gel zirconia films, ion bombardment with an analytical beam could affect materials being studied. The sol-gel thin films contained hydrogen, carbon, and excess oxygen. It was shown that even at -100°C , the irradiation of 280 keV noble gas ions, such as Ar and Xe ions, produced dramatic densification in the films. The densification was characterized by the loss of gaseous hydrogen, carbon, and oxygen-based chemical groups [3,7]. Fig. 5 shows RBS spectra from a 80 nm zirconia sol-gel film coated on (100) silicon wafer bombarded with 3.55 MeV He^{2+} ions to 20 and 330 μC . A small increase (10%) in the height of zirconium signal, as the collected charge accumulated from 20 to 330 μC , indicates some densification induced by the analytical beam alone. We noted that most of the densification took place during the first 60 μC of data acquisition and that the 3.55 MeV He ion beam induced the release, for the most part, hydrogen species. The densification is much less than the maximum densification achieved by 280 keV noble gas ions with a 50% increase in the zirconium RBS signal height.

8. Sample heating effect on ion beam analysis

The capability of performing the *in situ* ion irradiation experiment at high temperatures is important for radiation damage and ion beam induced epitaxial growth study. However, the detection of backscattered particles is limited by the unwanted heating on the surface barrier

detectors from the heated sample stage. The detectors have excessive leakage current once their temperatures reach above 50°C. We tested the sample heating effect on the detector performance. As the sample temperature was raised from room temperature through 60°C to 100°C (with heating power of 30 W), no significant change in the channeling spectrum was observed, as shown in Fig. 6 for the 6H-SiC crystal. The small increase in dechanneling yield in the spectrum was due to an increase in lattice thermal vibrations. The energy resolution of the detector gradually degraded with the increase in the sample temperature from 120 to 300°C. The spectrum became unusable as the sample temperature reached 300°C (with heating power of 130 W) due to leakage current in the detector. Since there was no direct thermal contact between the sample stage and the detector, the temperature rise in the detector was due solely to the thermal radiation heating effect. The heating took much longer to reach thermal equilibrium on the detector when the sample temperatures were below 300°C. By blocking the detector with the shutter when not taking data, the detector heating was partially reduced. We expect that the heating effect on the backscattering detection can be effectively overcome by shielding the detector and cooling it and its surroundings. The development of detector cooling capability is in progress.

9. Conclusions

The *in situ* ion beam facility at the IBML has been developed for the purpose of measuring the composition and crystallinity of materials irradiated with a 100-400 keV ion beam in a fast, efficient, controlled, and quantitative manner. It plays a vital role in radiation damage studies of ceramics being conducted at LANL. Radiation effects in several ceramic materials have been studied using this facility. Many useful experimental techniques, dealing with *in situ* ion beam analysis and ion irradiation, have been developed for radiation damage studies. Axial channeling directions with acceptably low minimum yields have to be chosen for the detection of radiation damage in single crystals. The selected channeling directions also need to satisfy the requirement of a small incident angle for irradiation in order to minimize surface sputtering. The surface charging on insulating materials can be minimized with proper coating of thin conducting materials. For many radiation resistant ceramics, high doses (8×10^{16} He/cm²) of MeV analytical

He ion beams show no observable radiation damage or chemical effects in the near surface region, where significant lattice disorder is produced only by the 100-400 keV irradiating beams. Detector heating due to thermal radiation from the heated sample stage can be overcome by properly shielding and ultimately cooling the detector.

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Figure captions

Figure 1 Schematic drawing of the sample stage installed within the *in situ* ion beam chamber in connection with both analytical and irradiation beamlines.

Figure 2 Aligned backscattering spectra from a c-cut MgTiO_3 single crystal obtained along the $\langle 0001 \rangle$ and $\langle 1014 \rangle$ channeling axes, along with the random spectrum.

Figure 3 Aligned backscattering spectra obtained from a (100) MgAl_2O_4 single crystal, coated with an 1 nm Au film, along the $\langle 110 \rangle$ channeling direction, before and after the irradiation of 370 keV Xe ions at -50°C to $2 \times 10^{15} \text{ Xe/cm}^2$.

Figure 4 Aligned backscattering spectra from a c-cut 6H-SiC single crystal along the $\langle 0001 \rangle$ channeling direction, obtained after bombarded with a 2 MeV analytical He^+ ion beam to 40 and 400 μC .

Figure 5 Backscattering spectra from a sol-gel zirconia thin film coated on (100) Si wafer, subject to the bombardment of a 3.55 MeV analytical He^{2+} ion beam to 20 and 330 μC .

Figure 6 Aligned backscattering spectra from a c-cut 6H-SiC single crystal along the $\langle 1012 \rangle$ channeling direction, obtained when the sample temperatures were 60 and 100°C .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6