PROTON ELASTIC SCATTERING ANALYSIS OF C, N AND O COMPOSITION IN MATERIALS

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ABSTRACT

Proton elastic scattering at energies around 2.0 MeV was used to determine the concentration of oxygen in a Y-Ba-Cu-O compound, nitrogen in a TiN film on steel substrate, and carbon and oxygen in a thin Mylar film. Proton scattering from light elements in this energy range exhibits non-Rutherford scattering cross section, which is enhanced by a factor of 4 to 7 relative to the Rutherford scattering cross section. Thus the sensitivity for the light element detection is considerably larger than that obtained by He^+ ion scattering. Quantitative analysis by proton scattering is discussed and compared with other methods.

Keywords: Proton elastic scattering Light element detection

1 INTRODUCTION

In the low ion energy range, there are mainly five ion beam analysis (IBA) techniques for material research, namely Rutherford backscattering (RBS), ion channeling, elastic recoil detection (ERD), nuclear reaction analysis (NRA) and particle induced X-ray emission (PIXE).[1,2] Among these, RBS is probably so far the most commonly used technique. Over the past years, He^+ ions of a few MeV had been almost exclusively used as probe ions in the RBS technique. However, He^+ RBS is not sensitive to light elements in a heavy element matrix. In view of this, proton beams of a few MeV would frequently be needed as a probe for thick or thin samples, because protons are advantageous over the He particles in terms of the penetrability, energy straggling, target damage and sensitivity for light element detection. One of the main difficulties to use proton elastic scattering as an analytical tool is that the interpretation of the proton scattering spectra is usually not as straightforward as that of the He^- ion RBS, because, unlike the monotonic energy dependence of the He^+ RBS cross section, the proton scattering cross section normally has resonance peaks. Moreover, proton elastic scattering cross sections were measured mostly in the 50′s and 60′s.[3-5] Most of the data are published in curves rather than tabulated forms and there are discrepancies among the data by different authors. However, the recent measurements of proton scattering cross sections of light elements, such as C, N, O and Si in Ref [6,7], have greatly facilitated light element detections with the PES technique.

Because the shape of elastic scattering excitation curves sometimes changes rapidly with the scattering angle, it is necessary for us to measure the scattering cross sections. The cross sections were generally expressed in terms of the ratios to the Rutherford values. With these ratios the computer simulation codes used in RBS analysis can be applied to the PES measurement. In this paper, the data of the PES cross section ratios of C, N and O at 170° are presented and some examples are given to demonstrate the capability of PES in compositional analysis of light elements.

2 EXPERIMENTAL

Two standards were used for the PES cross section measurements. A 15 $\mu g/cm^2$ layer of La_2O_3 on a 20 $\mu g/cm^2$ carbon foil was prepared by vacuum deposition. A 200 nm TiN_x layer on a graphite substrate was prepared by 2 keV Xe^+ ion beam enhanced deposition[8]. The characteristics of the standards were carefully checked by 2 MeV He^+ RBS before and after the proton measurements. No significant changes were detected in the standards during the experiments.

The measurements were carried out in a conventional IBA chamber at the 4 MeV pelletron in SINR. The proton energy was calibrated with the $^{27}Al(p,\gamma)^{28}Si$ resonances. A surface barrier silicon detector with an energy resolution of 16 keV was placed at the scattering angle of 170° to detect the backscattered ions. The target-to-detector distance was 80 mm and the aperture in front of the detector was Φ3 mm. The beam was 1 mm in diameter and the typical beam current was 5 nA.

The samples for compositional investigation were (a) a YBaCuO superconductor film on $SrTiO_3$ substrate which was fabricated by RIBC-I apparatus[9], (b) the TiN_x layer on steel substrate prepared by IBED method[8] and (c) a 1.5 μm self-supported Mylar foil.

3 RESULTS AND DISCUSSION

The measurements were performed with 2.0 MeV protons. The reason for this choice is that within a relatively broad energy range the scattering cross sections of all the three elements depend little on the proton energy[6,7]. This fact may greatly facilitate the evaluation of element depth profiles. By measuring the standards, the enhancement factors k, i.e. The ratio of PES cross sections of C, N and O to their Rutherford values, were determined. For 2.0 MeV protons and 170° scattering angle it was obtained that $k = 6.5 \pm 0.1$, 5.9 ± 0.2 and 4.1 ± 0.1 for C, N and O, respectively, which are in good agreement with those in Ref [6,7]. The details of the results have been published elsewhere.[10]

Fig.1 shows the 3.4 MeV He^+ RBS spectrum (A) and 2.0 MeV PES spectrum (B) of the Y–Ba–Cu–O film on a $SrTiO_3$ substrate[9]. In the He^+ RBS spectrum, the signals from Y, Ba and Cu are clear and well separated. However, the oxygen signal can hardly be seen because of its small Rutherford scattering cross section and high background of the low energy region. However, by using the 2 MeV proton beam, the cross section for oxygen is enhanced by a factor of 4 over Rutherford cross section at $\theta = 170^{\circ}$. Also, because of a larger kinematic factor, the oxygen signals appear at the PES spectra and a much clear oxygen signal step can be seen.

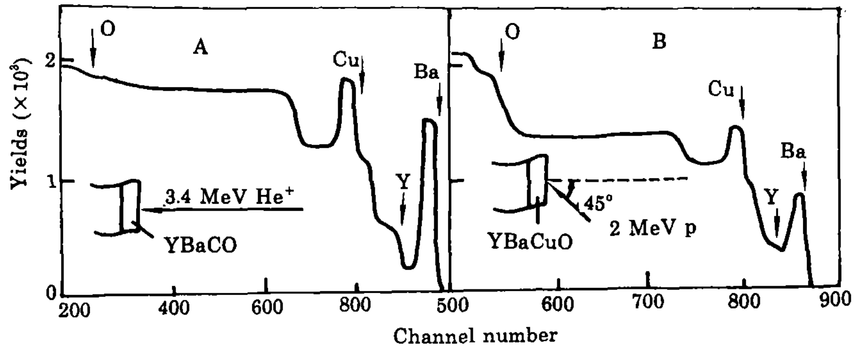

Fig.1 3.4 MeV He RBS spectrum (A) and 2.0 MeV PES spectrum (B) of a YBaCuO film on $SrTiO_3$ substrate

By combining the He^+ ion RBS and PES, the composition analysis is straightforward. The ratios of Y:Ba and Cu:Ba can be calculated from He ion RBS. It turns out that Y:Ba:Cu = 1:1.89:2.87. The oxygen composition fraction can be calculated by comparing the spectrum surface height of oxygen with that of Ba in the proton scattering spectrum, which gives the ratio of O:Ba = 3.6:1. Thus the stoichiometry of the superconductor film is Y:Ba:Cu:O = 1:1.89:2.87:6.80, which is slightly smaller than that of normal superconductor 1–2–3 phase compound. Zero-resistivity of this sample was achieved at 86 K. In the calculation, both the proton and He^- ion scattering from Y, Ba and Cu were assumed to follow the Rutherford cross section.

The nitrogen analysis was demonstrated with the thick TiN_x film on a steel substrate. As shown in Fig.2A, the nitrogen can hardly be resolved from the high background in the 2 MeV He^- RBS measurement. But in Fig.2B, because of the greater cross section and larger kinematic factor of the PES technique, higher N yields are found at the higher energy region. Calculation using the surface height of Ti an N signals shows that the surface composition of this TiN film is Ti:N = 1:0.94. In the calculation, care has to be taken since the deviation of proton–Ti elastic scattering cross section from Rutherford cross section might not be negligible in the low MeV proton range.[11] The approximate TiN layer areal density estimated from the energy shift of the steel edge is 6.1×10^{19} atoms/cm^2 (corresponding to 3.0 μm for stoichiometric TiN with specific gravity of 5.22 g/cm^3. Moreover, the composition profile can be obtained if computer simulation is used.

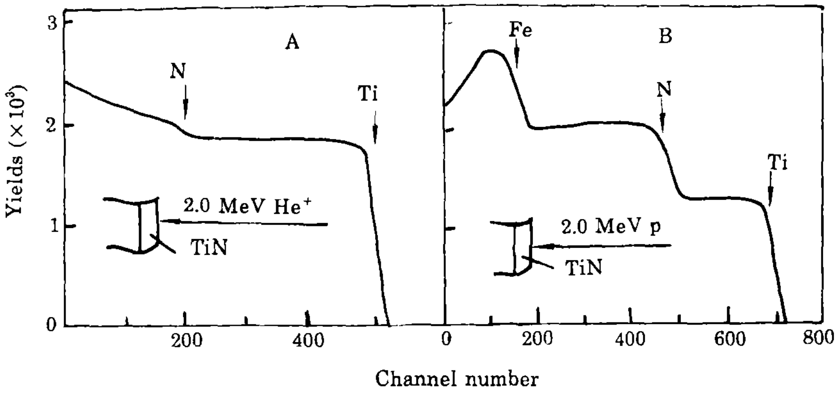

Fig.2 Energy spectra for 2.0 MeV He (A) and protons (B) incident on a thick TiN film deposited on steel substrate

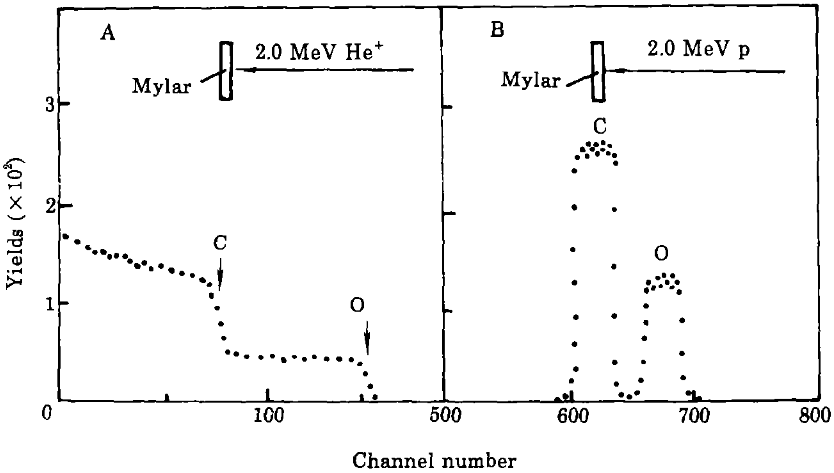

Fig.3 Energy spectra of a self–supported Mylar foil from 2.0 MeV He RBS (A) and PES (B) analysis

In the case of 1.5 μm Mylar film, it is known that energetic ions (>1 keV/u) can transfer a large amounts of energy to the polymer through electronic excitation, which creates breaking bonds and subsequent molecular emission[12]. When IBA technique is applied to polymer studies, care must be taken to ensure that ion beam induced changes do not alter the chemical composition of polymer. From this point of view, PES would be more favorable than He^+ RBS. Fig.3 compares two spectra of Mylar film for a total charge collection of 1 μC for both 2.0 MeV He^+ RBS and PES analysis. In Fig.3B, the C and O signals are well separated from each other. If we utilize p–p scattering for hydrogen detection and PES for the others simultaneously, atomic ratio of the elements in a thin polymer can be determined. The O/C and H/C ratios obtained agreed well with the nominal composition (within 3%). In order to check ion beam induced damage to the Mylar foils, a series of RBS and PES measurements were done with varying dose of the protons and He^+ ions. The O/C ratio determined with the 2 MeV He^+ beams differed considerably from each of the measurements. However, in the PES measurements no significant composition changes were observed (up to a total dose of $5\times10^{15}cm^{-2}$), although the areas of H, C and O signals decreased slightly (3%) due to erosion of the foil. As compared with He^+ RBS, one of the advantages with MeV protons is to produce less damage to the samples.

4 CONCLUSION

The examples shown here demonstrate that the low energy (below 2.5 MeV) proton elastic scattering is a useful technique for detection of light elements, such as C, N and O in materials.

PES retains most of the advantages of the He^+ ion RBS, such as speed, simplicity, non–destruction and capability of depth profiling. But PES is much more sensitive to light elements than He^+ ion RBS. As compared with He^+ ions, protons have a larger accessible depth and create less radiation damage. The latter factor might be important for certain materials such as polymer. However, the mass resolution and depth resolution of protons are lower than that of He^+ ions. Besides, care has to be taken in interpreting the PES spectrum not letting the proton inelastic scattering confuse the interpretation.

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