Simultaneous depth profiling of constituents and impurities by elastic proton scattering in amorphous hydrogenated silicon films

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Depth profiles of various constituents and impurities of thin films were obtained simultaneously by a nuclear coincidence method. The energy spectrum of elastically scattered 12 MeV protons, measured by a high-resolution magnetic spectrometer, was used for constituent identification and total content determination. Constituents of interest were selected by software pulse height discrimination and their depth profiles were obtained from the recoil energy spectrum, measured by a surface barrier detector telescope. Thin films of Teflon, of carbon, and of amorphous hydrogenated silicon were measured. The best possible depth resolution is about 20 nm for carbon and is limited by the beam energy spread and the energy resolution of the solid state detectors.

The quantitative study of alloy films based on amorphous hydrogenated silicon (*a*-Si:H) requires the knowledge of the average concentration and of the concentration profiles of the film constituents.[1] In the instance of $a\text{-Si}_{1-x}\text{Ge}_x$:H,F the constituents range from very light (H) to intermediate (Ge) elements and include impurities such as C, N, and O. We report here the first use of a coincidence method of elastic proton scattering, measured in transmission mode, which provides such profiles.

A classical tool for depth profiling has been Auger electron spectroscopy[2] (AES) and secondary ion mass spectroscopy (SIMS) which have excellent depth resolution[3] of down to 1 nm at the sample surface and some 10 nm at a depth of 0.4 μm.[4] AES, however, is not applicable in the case of hydrogen. The sensitivity of both methods is, in general, a function of the chemical structure of the film under study, which makes the absolute calibration difficult. Another problem may arise when analyzing fluorine content, where erosion due to ion bombardment can occur and the measured concentrations may be underestimated.

In order to overcome some of these problems a number of nuclear methods for chemical analysis of thin films have been proposed. With hydrogen, for example, depth resolutions, measured at the sample surface, of about 4 nm and 50 nm were reported with a nuclear reaction technique[5] and a nuclear coincidence measurement,[6,7] respectively. Other elements can be investigated by Rutherford backscattering (RBS) of low-energy alpha particles with a depth resolution of 5–30 nm,[8] depending on the geometry. It has been recognized that at grazing incidence a good depth resolution is obtained in the energy spectrum of the recoil particle (ERD, elastic recoil detection[9–11]). In the last two techniques spectra from different constituents in the film, or in the substrate, may overlap. An elegant way to separate these spectra is the introduction of a time-of-flight setup for particle identification.[12]

We have recently shown[13] that at intermediate energies light particles, like protons, can be used in a single arm experiment to measure the content of thin-film constituents with high precision. Due to the low mass of protons, samples can be measured in transmission. However, this technique provides only a modest depth resolution. For typically 1-μm-thick *a*-Si,Ge:H,F films on 8-μm-thick Al foils the resolution was 0.6 μm for F and Al.[14] In this letter we report how the depth resolution can be increased in a double arm arrangement by a factor of 10 to 20, depending on the mass of the measured element. A high-resolution magnetic spectrometer in one arm analyzes the elastically scattered protons for element identification and for measurement of total concentration. A surface barrier detector telescope in the second arm measures the energy, and thus the depth profile, of elements recoiling from the target. Elements are selected by software pulse height discrimination. Several elements can be measured simultaneously, i.e., in one single run.

The measurement geometry is shown in Fig. 1. A beam of 12 MeV protons from the Princeton Cyclotron was used along with a high-dispersion, high-resolution, magnetic

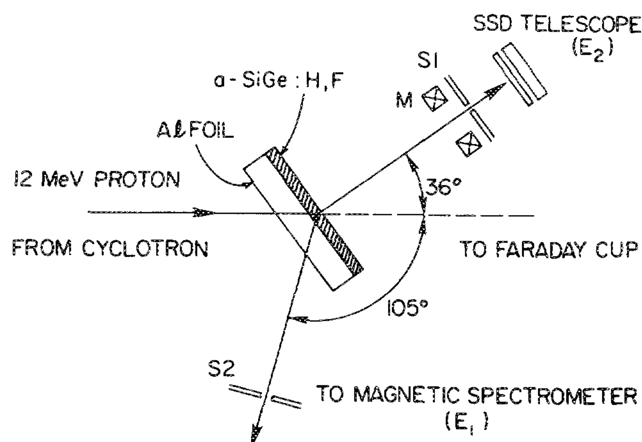

FIG. 1. Schematic of the experimental setup showing the target, the solid state detector (SSD) telescope, and the magnetic spectrometer (S = slits, M = small magnet).

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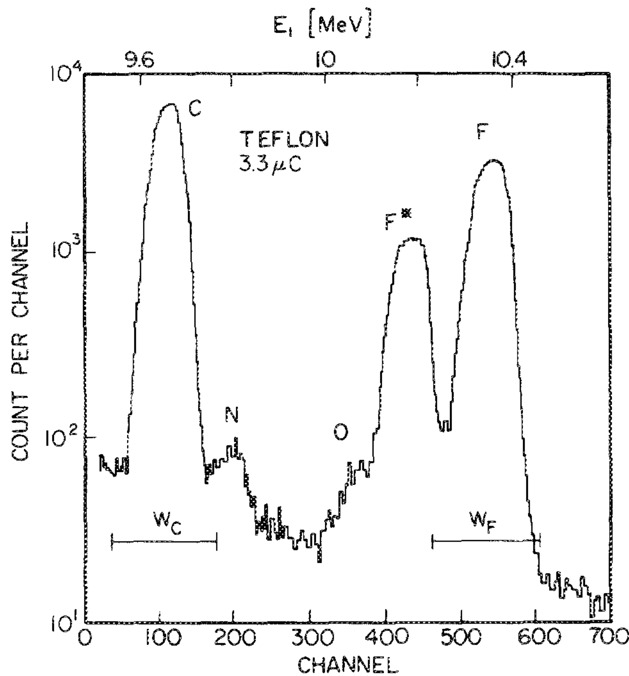

FIG. 2. Proton energy spectrum from a Teflon calibration target. F* denotes an excited state of the fluorine nucleus which is shifted by 197 keV with respect to the elastic peak.

spectrometer to detect the protons elastically scattered from the target constituents. The spectrometer observed the scattered protons at a large angle (105°) in reflection from the target, while a solid state detector (SSD) telescope at 36° observed the recoiling target nuclei. A heavy ion surface barrier detector (ORTEC EF-30-100-60) with an energy resolution of 30 keV was used. The angles were chosen to give the recoil nuclei enough energy (several hundred keV) to be observed above the noise in the uncooled SSD telescope. A small permanent magnet in front of the SSD counter separates out most of the low-energy secondary electrons. The sample shown in Fig. 1 is a 1.5-μm-thick a-$Si_{0.78}Ge_{0.22}$:H,F film which was deposited on an 8-μm-thick Al substrate film by radio frequency glow discharge in a SiF_4, GeF_4, and H_2 source gas mixture.[15] For calibration purposes thin polymer foils and a free-standing carbon film (area density 40 μg/cm^2, thickness approx. 0.2 μm) were employed.

Figure 2 shows the energy spectrum (E_1) for protons when measuring a 12-μm-thick Teflon foil [fluorinated ethylene propylene, $(C_5F_{10})_n$]. Since the energy of the scattered protons depends on the mass of the target nuclei, the fluorine and carbon signals are well separated. The carbon and fluorine peak windows (W_C and W_F, respectively) in the E_1 spectrum can be used to gate the SSD spectrum and to select only the SSD signal due to C or F recoils. The effect of this gating procedure is seen in Fig. 3. Figure 3(a) shows the total SSD spectrum, while Fig. 3(b) shows the same spectrum with the requirement that the spectrometer see protons scattered from carbon (W_C) only. The path length of each carbon recoil nucleus through the film depends on its initial location. Thus the carbon SSD coincidence spectrum maps out the carbon concentration profile. A calibration that takes the energy loss dE/dx into account[16] yields the distance scale indicated on Fig. 3(b). Note that dE/dx depends on energy, so that the position x does not scale precisely with channel number. The computed depth scale is valid at the sample surface.

A complete suppression of the proton peak seen in Fig. 3(a) and a strong reduction of background noise in the SSD spectra was obtained by the additional requirement that the time difference between the two detector signals be smaller than a few tens of nanoseconds.

Figure 4 shows the results from the fluorinated amorphous silicon sample a-$Si_{0.78}Ge_{0.22}$:H,F. The fluorine recoil spectrum is depicted in Fig. 4(a) and the carbon and oxygen spectra in Fig. 4(b). The corresponding depth scales are also given. The dose and time for this run were 54 μC of accumulated charge and 90 min, respectively.

The recoil energy spectra (E_2) were calibrated with a standard ^{241}Am α-particle source (5.5 MeV). The calibra-

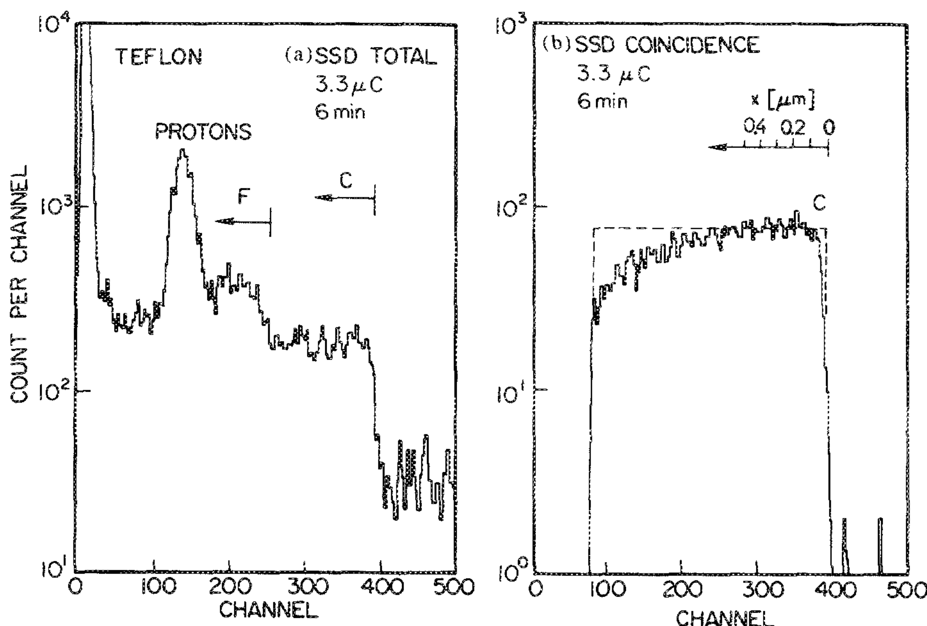

FIG. 3. Recoil energy spectra from a Teflon target for (a) all recoil particles and (b) for those in coincidence with protons scattered off carbon.

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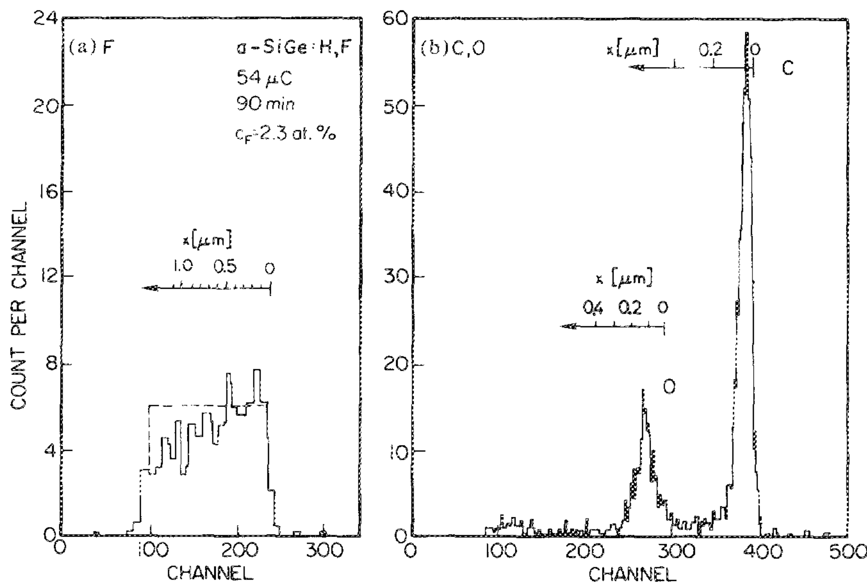

FIG. 4. Solid state detector (SSD) spectra for a fluorinated amorphous silicon target a-$Si_{0.78}Ge_{0.22}$:H,F showing (a) the fluorine recoils and (b) the oxygen and carbon recoils. The carbon and oxygen signals are due to surface contamination.

tion factor for the channel numbers in Figs. 3 and 4 is 5.7 keV per channel. The maximum recoil energy values at 36° are 2.284 MeV for C and 1.478 MeV for F. Their energy loss dE/dx at these energies are 1.4 and 0.7 MeV per μm of silicon, respectively. Therefore, the depth resolution near the film surface for C is expected to be about twice the one for F. The measured values which were determined from the slope of the spectra in Figs. 3(b) and 4(a) are 70 nm for C and 150 nm for F.

Multiple scattering leads to a spreading out of the recoil ions around the detector angle of 36° for those originating deep in the film. This produces the decrease in the count rate at large x values of Fig. 3(b), even though the carbon concentration is constant throughout the Teflon foil, as indicated by the dashed line. Similarly, the fluorine recoil spectrum of Fig. 4(a) indicates that the fluorine concentration throughout the amorphous silicon film is constant. From calibration of the F peak in the elastically scattered proton spectrum the F content was found to be 2.3 at. % for this film. The carbon and oxygen peaks of Fig. 4(b) are due to surface contamination.

The measured depth resolutions for C and F are limited, first, by the beam energy spread and the energy straggling of the incident protons and, second, by the energy resolution of the solid state detector. The first contribution can be minimized by reducing the substrate and film thickness. Using the above mentioned calibration factor the detector resolution of 30 keV limits the depth resolution of carbon to 21 nm. To obtain a reasonably accurate depth profile the concentration should at least be 1 at. %. This method is not appropriate for depth profiling of hydrogen due to the equal mass of scattered and recoiling ion in this case. Migration or loss of F, which is present at a percent level, is not likely to occur upon irradiation with proton doses used here, but this should be checked by taking spectra in consecutive runs. Proton beams of lower energy from small accelerators could be used at the expense of higher energy straggling and thus reduced depth resolution.

In summary, we have presented a new technique for depth profiling of constituents in thin films by elastic proton scattering. Using coincidence requirements between the elastically scattered proton and the recoil ions, several depth profiles could be monitored simultaneously. The depth resolution depends on the constituent mass and is limited by the beam energy spread and the solid state detector resolution.

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[1]G. Foti, J. W. Mayer, and E. Rimini, in *Ion Beam Handbook for Material Analysis*, edited by J. W. Mayer and E. Rimini (Academic, New York, 1977), pp. 21–65.
[2]*Characterization of Solid Surfaces*, P. F. Kane and G. B. Larrabee, eds. (Plenum, New York, 1976).
[3]C. W. Magee and E. M. Botnick, J. Vac. Sci. Technol. **19**, 47 (1981).
[4]P. Williams, C. A. Evans, Jr., M. L. Grossbeck, and H. K. Birnbaum, Anal. Chem. **48**, 964 (1976).
[5]W. A. Lanford, H. P. Trautvetter, J. F. Ziegler, and J. Keller, Appl. Phys. Lett. **28**, 566 (1976).
[6]P. Paduschek and P. Eichinger, Appl. Phys. Lett. **36**, 62 (1980).
[7]N. Fukada, T. Imura, A. Hiraki, T. Itahashi, T. Fukuda, and M. Tanaka, Jpn. J. Appl. Phys. **21**, L532 (1982).
[8]J. F. Ziegler and J. E. E. Baglin, J. Appl. Phys. **42**, 2031 (1971).
[9]I. P. Chernov, V. N. Shadrin, Ju. P. Cherdantsev, V. N. Sulema, L. V. Chramova, T. P. Smirnova, and V. I. Belyi, Thin Solid Films **88**, 49 (1982).
[10]J. L'Ecuyer, C. Brassart, C. Cardinal, J. Chabbal, L. Deschen, J. P. Labrie, B. Terreault, J. G. Martel, and R. St-Jacques, J. Appl. Phys. **47**, 381 (1976).
[11]D. C. Ingram, A. W. McCormick, and P. P. Pronko, Nucl. Instrum. Methods B **6**, 430 (1985).
[12]R. Groleau, J. F. Currie, M. R. Wertheimer, and J. E. Klemberg-Sapieha, Thin Solid Films **136**, 85 (1986).
[13]R. Schwarz, S. Wagner, R. T. Kouzes, and R. D. Wieting, Appl. Phys. Lett. **46**, 552 (1985).
[14]R. Schwarz, Y. Okada, S. F. Chou, J. Kolodzey, D. Slobodin, and S. Wagner, Abstract No. EP2.5, presented at the MRS Spring Meeting, Palo Alto, April 1986.
[15]J. Kolodzey, S. Aljishi, R. Schwarz, D. Slobodin, and S. Wagner, J. Vac. Sci. Technol. A **4**, 2499 (1986).
[16]J. F. Ziegler, *Stopping Cross Sections for Energetic Ions in all Elements* (Pergamon, Oxford, 1980).

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