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Determination of the hydrogen concentration in silicon nitride films with the resonant nuclear reaction $^1H(^{15}N, \alpha\gamma)^{12}C$

E. J. EVERS
R. J. Van de Graaff Laboratory, Rijksuniversiteit Utrecht, P. O. Box 80.000, 3508 TA Utrecht, The Netherlands

and

F. H. P. M. HABRAKEN
Dept. of Technical Physics, Rijksuniversiteit Utrecht, P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

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Abstract—The resonant nuclear reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ at resonance energy $E(^{15}N^{2+}) = 6.40$ MeV has been used to investigate the hydrogen concentration in silicon nitride films.

This method is very suitable to determine hydrogen concentration profiles with a good depth resolution (~ 5 nm) over a large depth (~ 2 μm) and has a sensitivity of a few tenth of an atomic percent.

1. INTRODUCTION

IN RECENT years the importance of hydrogen as dangling-bond terminator in all kind of semiconducting and insulating materials has been recognized. However, the low atomic number of hydrogen makes its detection unaccessible to the conventional electron spectroscopic techniques as Auger electron spectroscopy and X-ray photoelectron spectroscopy and to nuclear techniques, based on elastic scattering as Rutherford Backscattering Spectroscopy (RBS). An exception is the proton–proton scattering technique [1, 2], but this method imposes high demands upon sample preparation. A nice method for hydrogen detection is of course infrared absorption spectroscopy, either in the single transmission mode or making use of multiple internal reflection. The method yields information about binding states, but quantification is not always simple, whereas no spatial information can be obtained.

Recently nuclear reaction analysis (NRA) of thin films has gained considerable interest. LANFORD *et al.* [3] have shown that the resonant nuclear reaction $^1H + ^{15}N$ is very suitable for hydrogen depth profiling in solids. Up to now we used the method to measure the hydrogen concentration in silicon (oxy)nitride films, prepared by LPCVD [4] and by thermal nitridation of thin silicon dioxide films [5].

In this paper we describe the features of the method and the experimental set-up and we illustrate it with measurements in LPCVD silicon nitride films.

2. METHOD

The hydrogen concentration [H] is measured by nuclear reaction analysis using a $^{15}N^{2+}$ beam from our tandem Van de Graaff accelerator.

When a ^{15}N nucleus with a laboratory energy of 6.40 MeV collides with a proton at rest, the resonant reaction $^1H(^{15}H, \alpha\gamma)^{12}C$ occurs, yielding an α-particle and a characteristic 4.43 MeV γ-ray. This resonance has a width of only 12 keV, which results in a depth resolution in silicon (oxy)nitrides of about 5 nm. The off-resonance cross section is about two orders of magnitude smaller than the peak cross-section [6].

[1] B. L. COHEN, C. L. FINK and J. H. DEGNAN, *J. Appl. Phys.* **43**, 19 (1972).
[2] P. PADUSCHEK and P. EICHINGER, *Nucl. Instr. Meth.* **191**, 75 (1981).
[3] W. A. LANFORD, H. P. TRAUTVETTER, J. F. ZIEGLER and J. KELLER, *Appl. Phys. Lett.* **28**, 566 (1976).
[4] F. H. P. M. HABRAKEN, E. J. EVERS, G. A. P. ENGELBERTINK and A. E. T. KUIPER, *Proc. Insulating Films on Semiconductors, Eindhoven* 1983, Eds J. F. VERWEIJ and D. R. WOLTERS, p. 121. North-Holland, Amsterdam (1983).
[5] F. H. P. M. HABRAKEN, E. J. EVERS and A. E. T. KUIPER, *Appl. Phys. Lett.* **44**, 62 (1984).
[6] C. ROLFS and W. S. RODNEY, *Nucl. Phys.* **A235**, 450 (1974).

Thus when bombarding a sample with 6.40 MeV ^{15}N nuclei and measuring the yield of the 4.43 MeV γ-rays, we get a measure for the hydrogen content of the topmost layer of the sample. If we increase the beam-energy (which can be done accurately in steps down to 5 keV) the nuclear reaction does not take place at the surface in a significant amount, but at a certain depth, where the ^{15}N-ions have lost as much energy as to reach the resonance energy. Thus by stepwise increasing the beam energy and measuring the γ-yield after collecting each step a fixed amount of charge on the target, we can measure the hydrogen concentration profile through the film. Using the stopping cross-section tables of ZIEGLER [7] we can calculate the depth in the target from the difference between the actual beam energy and the resonance energy. With this reaction it is possible to scan upto a depth of about 2 μm, although the depth resolution becomes worse with increasing depth due to the spread in beam energy, which arises during the travel of the beam through the material (straggling). Apart from the straggling, whose influence is noticeable at depths larger than about 100 nm in silicon, the depth resolution is determined by the stopping power of the ions in the material, in which the hydrogen is detected. The larger the stopping power, which increases with the density and with the charge number of the material under investigation, the better is the depth resolution. In principle the depth resolution can be improved by bombarding the sample under a small angle with the surface.

The sensitivity of this nuclear technique is determined by the cosmic background radiation and by the non-zero off-resonance cross-section for the nuclear reaction. The latter results in a contribution to the measured γ-yield from the reaction of ^{15}N nuclei with hydrogen present at other depths than the probing depth. In practice the lowest hydrogen concentration, which can be detected, amounts to a few tenth of an atomic percent. To increase the signal-to-background ratio by increasing the ^{15}N-dose is not always possible because the samples appear not always stable under high-energetic ion bombardment (see Section 4).

3. EXPERIMENTAL

A schematic view of our set-up is given in Fig. 1. The target is positioned in a vacuum of about 10^{-6} Torr, such that it makes an angle of 45° with the beam direction. In order to avoid secondary electrons disturbing the measurement of the dose of the $^{15}N^{2+}$ ions, beam current is integrated at both the target and the insulated surrounding chamber. Two diaphragms are included in the set-up: the first one ($\varnothing$ 2 mm) is used to collimate the beam; the second one ($\varnothing$ 2.5 mm) has two functions: it stops ^{15}N-ions scattered from the first diaphragm and, since it is kept at a potential of -170 V it forms a barrier for secondary electrons to enter or leave the target chamber, which would disturb the current integration. The emitted γ-rays are detected with a 5 in. diameter NaI scintillation detector, positioned at an angle of 90° to the beam direction, about 2 cm from where the beam hits the target.

Beam currents used are typically 100 nA $^{15}N^{2+}$; measuring time per point varies from less than one to about 5 min.

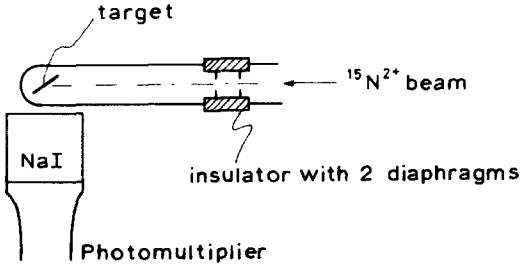

Fig. 1. Schematic plot of our set-up (see text).

[7] J. F. ZIEGLER, *Stopping Cross-Sections for Energetic Ions in All Elements*. Pergamon Press, New York, (1980).

4. Measurements

As an example we show hydrogen depth profiles in a LPCVD silicon nitride (Si_3N_4) film. These films were grown on crystalline silicon from SiH_2Cl_2 and NH_3 at 820°C and a total pressure of 200 mTorr using a NH_3/SiH_2Cl_2 gas flow ratio of 2.5 [8].

It is recognized that hydrogen atoms can be released from samples under the impact of high-energy ions [9]. Therefore it is essential to check the stability of the sample. We did this by measuring the 4.43 MeV γ-yield as a function of time and beam energy. Bombarding the sample with ions of 6.525 MeV, thus probing at a depth of 40 nm in the Si_3N_4 film, we found no change in [H] at a maxium dose of 1.7×10^{16} ions cm^{-2}, which is a dose sufficiently large for the measurement of a complete profile. Probing in the depth range 0–20 nm however, we observed a slow decrease in the γ-yield as a function of bombardment time.

Figure 2 shows the 4.43 MeV γ-yield as a function of the $^{15}N^{2+}$ beam energy (depth) for a 60-nm Si_3N_4 sample before and after annealing for 1 h at 900°C in vacuum. In the profiles we have omitted the large peak at the surface of the films originating from adsorbed water and/or hydrocarbons. The absolute concentration scale has been obtained by comparison of the γ-yield in the LPCVD film with that in a plasma deposited silicon nitride film with a known hydrogen concentration.

Neglecting the relative minimum in the profiles just below the surface, which is presumably due to the above mentioned outdiffusion effect, it is clear that the hydrogen concentration in both the as deposited and in the annealed film is constant throughout the film and amounts to about 3 atm. % in the unannealed film. Annealing for 1 h at 900°C in vacuum results in a loss of hydrogen. Finally, it appears that the hydrogen concentration falls within 10 nm to a very small value at the Si_3N_4/Si interface, which indicates that only very little or no hydrogen diffuses into the underlying silicon during growth or annealing.

5. Conclusion

Nuclear reaction analysis using the resonant reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ at resonance energy $E(^{15}N^{2+}) = 6.40$ MeV is a very suitable method to determine hydrogen concentrations in solid films.

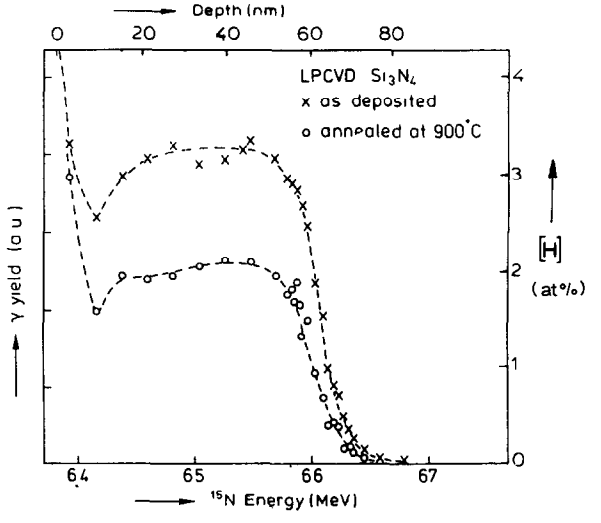

Fig. 2. The γ-yield ([H]) as a function of the ^{15}N beam energy (depth) for a 60-nm Si_3N_4 film, as measured before and after annealing for 1 h at 900°C in vacuum.

[8] F. H. P. M. Habraken, A. E. T. Kuiper, A. Van Oostrom, Y. Tamminga and J. B. Theeten, *J. Appl. Phys.* **53**, 404 (1982).

[9] J. P. Thomas, M. Fallavier and J. Tousset, *Nucl. Instr. and Meth.* **187**, 573 (1981).

If enough attention is paid to especially instability effects in the films, hydrogen concentrations down to a few tenth of an atomic percent can be measured accurately with a good depth resolution, at least in atomically smooth films.

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