

Hydrogen detection near surfaces and shallow interfaces with resonant nuclear reaction analysis

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Abstract

This review introduces hydrogen depth profiling by nuclear reaction analysis (NRA) via the resonant $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ reaction as a versatile method for the highly depth-resolved observation of hydrogen (H) at solid surfaces and interfaces. The technique is quantitative, non-destructive, and readily applied to a large variety of materials. Its fundamentals, instrumental requirements, advantages and limitations are described in detail, and its main performance benchmarks in terms of depth resolution and sensitivity are compared to those of elastic recoil detection (ERD) as a competing method. The wide range of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA applications in research of hydrogen-related phenomena at surfaces and interfaces is reviewed.

Special emphasis is placed on the powerful combination of $^1\text{H}(^{15}\text{N},\alpha\gamma)^{12}\text{C}$ NRA with surface science techniques of *in-situ* target preparation and characterization, as the NRA technique is ideally suited to investigate hydrogen interactions with atomically controlled surfaces and intact interfaces. In conjunction with thermal desorption spectroscopy, ^{15}N NRA can assess the thermal stability of absorbed hydrogen species in different depth locations against diffusion and desorption. Hydrogen diffusion dynamics in the near-surface region, including transitions of hydrogen between the surface and the bulk, and between shallow interfaces of nanostructured thin layer stacks can directly be visualized. As a unique feature of ^{15}N NRA, the analysis of Doppler-broadened resonance excitation curves allows for the direct measurement of the zero-point vibrational energy of hydrogen atoms adsorbed on single crystal surfaces.

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Keywords: Nuclear reaction analysis; Hydrogen depth profiling; Surface and interface analysis; Hydrogen adsorption; Hydrogen absorption; Hydrogen diffusion

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Abbreviations: AES, Auger electron spectroscopy; BGO, Bismuth germanium oxide ($\text{Bi}_4\text{Ge}_3\text{O}_{12}$); CRB, cosmic radiation background; CVD, chemical vapor deposition; ERD(A), elastic recoil detection (analysis); DFT, density functional theory; FET, field effect transistor; FGA, forming gas annealing; HAS, helium atom scattering; H_{at} , atomic hydrogen; H-ERD(A), high-resolution elastic recoil detection (analysis); HIERD, heavy ion elastic recoil detection; HREELS, high resolution electron energy loss spectroscopy; IAEA, International Atomic Energy Agency; IRAS, infrared absorption spectroscopy; LAPW, linear augmented plane wave; LEED, low energy electron diffraction; LERS, low energy recoil scattering; MBE, molecular beam epitaxy; MOS, metal-oxide-semiconductor; NR(A), nuclear reaction (analysis); PSD, position sensitive detector; RBS, Rutherford backscattering; PIXE/PIGE, particle induced X-ray/gamma-ray emission; ROI, region of interest (energy integration window in γ -spectroscopy); SNICS, source of negative ions by Cs sputtering; SSBD, silicon surface barrier detector; SSD, solid state detector; STM, scanning tunneling microscopy; TC, transmission channeling; TD(S), thermal desorption (spectroscopy); TOF, time-of-flight; UHV, ultrahigh vacuum; UPS, ultraviolet photoelectron spectroscopy; XPS, X-ray photoelectron spectroscopy

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1. Introduction

The great wealth of surface and interface interactions of hydrogen and water has caught the keen attention of the Surface Science community for a long time [1–8]. The weak Van-der-Waals forces (and surface-catalyzed ortho-para conversion processes [9–16]) in the physisorbed state of molecular H_2 are of lasting fundamental interest, and recently heightened from the viewpoint of hydrogen in energy applications [17,18]. Dissociative chemisorption [19–24], surface diffusion, and reaction of adsorbed H atoms with coadsorbates enable hydrogenation catalysis and fuel cell reactions. Recombination of H_2 is important in astrophysics as well as in photocatalysis and electrochemistry. Hydrogen surfactant effects in epitaxy and passivation of semiconductor interfaces impact fabrication

and reliability of electronic devices. Adsorption of hydrogen or water can tremendously change the physical and chemical properties of the substrate surface, giving rise to work function shifts, relaxation lifting, reconstruction, conductivity, hydrophilicity, corrosion, etc. Owing to its light mass, the dynamics of hydrogen are subject to quantum effects that may influence the rate of reactions, diffusion, and surface penetration at low temperatures.

Many materials also exhibit volume solubility for hydrogen [25–27]. Bulk-dissolved hydrogen may dramatically affect the electrical and mechanical properties of its host [27–29]. Metal hydride formation, essential for hydrogen storage [18,30] and optically switchable windows [31–33], the embrittlement of technical alloys [34], getter pumping and H_2 -outgassing in the ultrahigh vacuum (UHV) environment [35,36], the permeation

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