Solid State NMR Spectroscopy

Subjects: Nanoscience & Nanotechnology

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Solid-state NMR relaxometry has established its position in food science, including the determination of moisture content, solid fat content and much more and shown to be complementary to traditional microscopic techniques in studying the phase morphology of blended materials used in semiconductive polymer-based devices .

Keywords: solid-state NMR spectroscopy ; magic angle spinning (MAS) ; thin films ; solvent-matrix interactions ; sensitivity boosting ; polarization enhancement

1. Introduction

Thin films have a massive impact on the modern era of technology and have gained unprecedented interest during the past years due to their versatile properties and potential applications [1][2][3][4][5]. This class of advanced materials is generally defined as a thin layer of material having a thickness that ranges from fractions of a nanometer (i.e., monolayer) to several micrometers [6][7]. Among the most commonly used physical deposition methods to prepare thin films are evaporation and sputtering techniques [8][9]. Thermal vacuum evaporation is the simplest technique to form thin amorphous films, such as chalcogenide films [10][11], which are widely utilized in memory-switching applications [12][13], phase change materials [14][15] and solar applications [16].

Even though physical deposition methods provide high-quality thin films, they require expensive equipment and are highly costly [6][7]. Hence, chemical deposition methods are sought as economically viable and widely used global methods for the production of thin films [6][7]. Among the paramount techniques used in chemical deposition is the sol–gel [17][18][19] route, which produces high-quality films with low equipment requirements. Additionally, among the other important chemical deposition techniques that have been widely applied are: chemical vapor deposition (CVD) [20][21][22][23], spin coating [24][25][26], dip coating [27][28], chemical bath deposition [29][30] and spray pyrolysis technique [31][32].

In order to tailor the final properties of thin films in a targeted application and obtain information on their morphology, chemical and physical properties, there is a dire and urgent need to carefully characterize such films. Several characterization techniques in the past have been deployed to analyze thin films [33][34][35], but only minor attention was given to solid-state NMR with its wide range of techniques [36]. NMR is a physical phenomenon based on the perturbation of the nuclear spin located in a strong external magnetic field using a weak oscillating magnetic field, which intern responds by an electromagnetic signal that is detected and transformed into spectra. When the oscillation frequency matches the intrinsic frequency of the targeted nuclei, resonance occurs; hence, valuable chemical information can be determined.

The alignment of the nuclear spins along the applied external magnetic field.

The perturbation of this alignment using a weak oscillating magnetic field.

The detection of the NMR signal (voltage induced in a detection coil).

The interactions between the active nuclear spins and the magnetic fields determine the line shape of the peaks, thus the overall broadness of the spectra. Therefore, different solid-state NMR techniques were developed, including newly designed pulse sequences, to suppress and eliminate the broadness in the spectra of solid materials [37].

The arising orientation-dependent nuclear magnetic interactions in immobilized solid states is from the restricted thermal motions and lack of rapid molecular tumbling. This insufficient mobility exposes different types of internuclear and orientation-dependent nuclear interactions that accommodate information on the local geometric and electronic structure. Solid-state NMR is capable of performing a variety of experiments on a wide range of nuclei to retrieve valuable information on the local geometric and electronic structure from the emerged orientation-dependent nuclear magnetic

interactions. The range of nuclei solid-state NMR is capable of measuring is not limited to the conventional nuclei for organic materials typical 1H [38][39][40][41] and 13C [42][43][44][45] nuclei for organic thin films, but extends in inorganic thin films to cover a huge portion from the periodic table such as 2H [46][47],

2. Recent Advancement in NMR Strategies and Hardware Design

Among the few thin-film samples measured by MAS NMR, all sample preparation methods used were based on scratching the sample off the substrate previous to the rotor packing [48][49][50][51][52], lift-off technique, which is mainly composed of the water-soluble buffer layer method [53], followed by the polymer transfer layer method [54] and stacking the rotor with proper size pieces of thin films [55]. Solid-state NMR measurements on thin films were only possible in static mode (without sample rotation); thus, high-resolution spectra were limited to samples without anisotropic interactions [56] [57]. The non-destructive property of MAS NMR leads to the development of new probe and coil designs capable of measuring thin films, including the disk MAS design present in Figure 5 [58]. The significant advantages of the disk MAS are summarized in its ability to characterize the thin film under the nondestructive MAS conditions and tracing the identical thin film undergoing ex situ experiments, such as annealing, discharging/charging and degradation [58].

Several groups were able to produce microcoils using lithographic methods, but despite all the efforts conducted, these approaches did not reach the mainstream production in NMR spectroscopy [59][60][61]. Several microcoil designs were introduced and tested previously, including the micro helix coil, planar micro helix coil, saddle coil, stripline design [62] and the microslot design [63]. The latter design has a comparable approach with the stripline one, which, in turn, alternates from the helical coil design. Planar helices microcoil designs suffer from several problems, including B1 field homogeneity, increase in RF shielding currents and windings of the microcoil, thus leading to a severe reduction in resolution and sensitivity and difficulty in implementing 2D NMR methods [64].

The stripeline coil is basically a 2D flat copper wire covered with symmetric ground planes from both sides to confine the RF radiation, reduce the RF field strength decay and keep it homogeneous. The applied RF current passes through the flat strip, and a generated RF field encircles the strip. The local current density is at maximum in the middle of the strip, particularly between the boundaries of the restriction, which results in a high RF field at the sample placed along the channel. The novel stripline probe technology proved to be valuable in studying thin films where it provided high sensitivity to detect highly mobile hydrogen species in photochromic thin films [65].

NMR spectroscopy has suffered from relativity low sensitivity, especially in detection methods due to the extremely low thermodynamic population difference between the nuclear spin levels. Different methods for improving the detection sensitivity of NMR have been developed based on mechanical detection, where the first successful application was called Magnetic Resonance Force Microscopy (MRFM) [66]. The force experienced by the nuclear magnetic dipole moment upon settling in an external gradient field is detected by the atomic force microscope cantilever by mechanical means, and thus sub-angstrom resolution may be reached from the cantilever deflection. The inhomogeneous magnetic field is created by introducing a small magnetic particle in an external magnetic field, which results in the variation of the Larmor resonance over the sample; thus, particular slices of the sample can be excited through the variation of the irradiation frequency or the position of the magnetic field gradient source.

The driving force for developing the MRFM was the possibility to detect a single spin, which could make it an important tool in quantum computation, the efforts were successful [67], and MRFM was developed not only to detect electrons [68] but also protons [69] and latter isotope selective nuclei in organic monolayers [70]. The advancements in MRFM continued with the advanced observation of magnetization, enhanced resolution and no gradient (BOOMERANG) technique [71], ending with the coupling of ultrasensitive MRFM with 3D image reconstruction to achieve magnetic resonance imaging with <10 nm resolution limit [72].

Although advanced solid-state NMR techniques and pulse sequences, including MAS, are not applicable in MRFM, an NMR approach based on force detection method for chemical investigations using relaxation times or chemical shifts was developed [73]. Quadrupole nuclei and low γ nuclei are the best candidates for high-resolution imaging since the external field gradient does not have a major sensitivity enhancement effect, thus leaving this enhancement to be determined by the local structure experienced by the nuclei [74]. In particular, applications for MRFM includes the fields of coatings, colloids and semiconductors [73][75].

The implantation of probes (radioactive ions) that are highly spin polarized is an effective technique to overcome the low number of nuclei for a measurable signal in nanoscopic systems [76]. Optical pumping is an advanced method for spin polarization, as it provides reproducible results even with a very high degree of spin polarization (10–100%). Additionally,

the need for extreme cooling of the ions is not compulsory in optical pumping since it depends on atom/ion interaction with circularly polarized laser beams. The transfer of polarization from the electron to the nucleus is completed via hyperpolarization interaction [77][78].

The beam exposed to optical pumping implants into the NMR sample after its passage through the polarization section. A continuous RF field is applied on the sample leading to the nuclear sub-level transitions at the resonance frequency, and the decrease in spin polarization as the change in β-decay asymmetry is recorded. The employment of a highly spin-polarized radioactive beam with β-NMR creates a novel nuclear method of detection that has enough sensitivity to detect the presence of a single probe nucleus and build up a typical spectrum [79]. Due to its novel features such as high magnetic fields and the ability to control the depth of implantation ranging between 2–200 nm, β-NMR found many applications in surface science [80], insulators [81], semiconductors [82][83], antiferromagnetics [84] and thin films [85][86][87][88][89].

The transfer of polarization from electrons spins to nuclear ones through hyperfine interactions is called hyperpolarization. Upon the relaxation of the electron spin temperature back to the thermal equilibrium after its exposure to external microwaves, nuclear spins are hyperpolarized, leading to a drastic enhancement in the obtained NMR spectra. The term dynamic nuclear polarization (DNP) was assigned to distinguish this scheme from alternative hyperpolarization methods [90].

DNP NMR spectroscopy has been successfully applied to materials research more than to other biological systems due to the fact that the experiments are conducted at cryogenic temperatures between 20 K and 110 K. At these cryogenic temperatures, maximum sensitivity enhancements are obtained since electron relaxation time is long enough for the polarization to be transferred to the nuclei. In the case of an ideal nuclear polarization transfer, the NMR signal could match the ESR one, and DNP NMR could find new applications in surface chemistry [90]. DNP NMR spectroscopy was recently applied on different types of thin films, including phosphorus-doped silicon [91], organolead halide perovskites [92] and organic semiconducting ones [93].

3. Conclusion

Solid-state NMR has established its position in different fields of science, starting from inorganic materials such as zeolites [94], inorganic polymers [95] and borane-phosphane [96] passing through biological [97] and biotechnological systems [98] such as carbohydrates [99], proteins [100], biomembranes [101] and plant cell wall [102], environmental chemistry [103], and ending up with material science, including metal organic frameworks [104], perovskites [105], organic semiconductors [106] and functional nanomaterials [107]. Solid-state NMR spectroscopy, with its diverse techniques and measured nuclei, offers a wide range of valuable information on the geometric and electronic structure of advanced thin-film materials. Solid-state NMR is a promising technique in resolving as yet missing aspects of the molecular structure, polymorphism, packing and dynamics of thin films. Sensitivity is a great issue in solid-state NMR, placing it on the border, but recent technical and hardware advancements brought solutions to this that provided molecular information beyond expectations.

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