Localized characterization of poly (vinylidene-fluoride trifluoroethylene) thin film structure via AFM-IR spectroscopy

Abstract

We report on a localized AFM-IR spectroscopy characterization of a Poly (vinylidene-fluoride-trifluoroethylene), PVDF-TrFE, thin film. By studying the correlation between topography and local IR spectrum mapping, the micro-structure and molecular orientation of the crystalline film was revealed down to the nano scale.

Keywords: PVDF-TrFE, localized infrared spectrum, chemical mapping, micro-structure

Introduction

Poly (vinylidenefluoride) (PVDF) and its copolymers exhibit appealing electrical properties, such as bi-stable polarization, piezoelectric and pyroelectric properties, which make them promising for applications in organic bioelectronics. Recently, there has been an increasing interest in tuning the electrical properties of PVDF and its copolymers by controlling the microstructure down to the nano scale.1-4 The PVDF polymer can crystallize in a quasi-hexagonal close-packed “β-phase” structure with the dipoles of all chains aligned with maximum spontaneous polarization, as shown in Figure 1. The β-phase structure is directly related to its ferroelectric, piezoelectric and pyroelectric properties. In this sense, acquiring high-resolution spatial images, highly-sensitive localized infrared (IR) spectrum and the corresponding chemical image of β-phase PVDF or its copolymers at the nano scale are critical for new applications of ferroelectric polymers, especially for applications in Medical diagnosis. Over the past few years, atomic force microscopy infrared spectroscopy (AFM-IR) has emerged to be a new technique that provides localized nano scale chemical analysis and compositional mapping.5,6 It would be interesting to use AFM-IR to study the correlation between localized topography and molecular structure in PVDF or its copolymers thin films.

PVDF thin film preparation

The thin film studied here was made of copolymer of 70% vinylidene fluoride and 30% trifluoroethylene–Poly (vinylidene-fluoride-trifluoroethylene) (PVDF-TrFE), by spin coating. The 70/30 P (VDF-TrFE) was dissolved in methyl ethylketene (MEK) to a 2.5% concentration. A 30-nm thick gold thin film was thermally evaporated onto a 5mm by 5mm square substrate of p-type silicon with a 300nm oxidized layer, in order to enhance the localized IR measurement signal collection. Then an 80-100nm thick P (VDF-TrFE) film was spin coated on the gold surface, followed by drying and annealing for its crystallization.

Results and discussion

As is shown in Figure 2A, the P (VDF-TrFE) thin film has very uniform morphology, with typical highly crystalline rice grains. The localized IR spectrum of the P (VDF-TrFE) thin film, targeting at single or several rice grain regions (marked with a red circle), is shown in Figure 1A. Previous research results showed there are four fingerprints for β-phase PVDF in the IR spectrum7 at 1071 cm⁻¹, 1176 cm⁻¹, 1398 cm⁻¹ and 1428 cm⁻¹ respectively, which stand for the C-C antisymmetric stretching, CF₃ antisymmetric stretching, CH₃ waggling and CH₂ bending stretch of all-trans (TT) structure. We imaged AFM topography in Figure 2B, and its corresponding chemical mapping of PVDF at the absorption peak of 1078 cm⁻¹ was acquired simultaneously. Figure 2C shows the mapping of the C-C antisymmetric stretching absorption band for the scan area of 3µm×3µm of the topographic image (Figure 1B). More information of relationship between morphology and molecular structure of the sample section could be investigated in the future studies.

Figure 1 (a) Schematic of a polymer chain with β-phase, (b) End view of the chain.
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Figure 2 (a) Localized nano scale IR spectra of P (VDF-TrFE) at a single or several rice grains regions; (b-c) the height image and corresponding chemical mapping image of P (VDF-TrFE) at the specific wavelength of 1078 cm⁻¹.

Conclusion

In summary, we fabricated highly crystalline P (VDF-TrFE) thin film by spin coating. The AFM-IR technique was applied to study the correlation between morphology and molecular microstructure. More research is still ongoing to acquire more comprehensive structure information from PVDF thin films. The AFM-IR technique could also be very useful for analyzing other polymer thin film and nano structures.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

References