



Substrate effects on crystal orientations and structures of poly(ethylene-ran-vinyl acetate) ultrathin films



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ABSTRACT

The crystal orientations and structures of poly(ethylene-ran-vinyl acetate) (EVA) ultrathin films (5, 10 nm) spin-coated onto three different substrates (piranha-cleaned, acetone-cleaned, and hexamethyldisilazane-treated Si wafers) were investigated by using atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GIXRD). The crystal orientations were found to be edge-on for all three substrates, and two crystal structures, orthorhombic and hexagonal, were observed. As the polar nature of the substrate decreases, the hexagonal structure disappears, and the orthorhombic structure becomes dominant. The preference for an edge-on orientation is attributed not only to the repulsive interactions between the polar vinyl acetate components and the nonpolar ethylene components but also to the wetting conditions, i.e., to the interactions between the polar vinyl acetate component and the substrates. The formation of the hexagonal structure arises from the gauche defects of the ethylene chains. From these results, we discuss the interfacial properties that determine the preferred crystal orientations in thin films, and the effects of the interactions between the polar vinyl acetate components and the substrates on the chain conformations of the ethylene segments.

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1. Introduction

The structures and properties of polymer thin films can be different from those of thick films and bulk materials [1–15]. One important aspect of polymer crystallization under spatial confinement is the crystal orientation. Two crystal orientations are generally encountered in experiments. In the flat-on orientation, the chain axes of the lamellae are normal to the substrate, whereas in the edge-on orientation the chain axes of the lamellae are parallel to the substrate. A preferred crystal orientation arises in thin films because during crystallization the lamellae cannot rotate freely in their confined spaces. It is known that the orientations of lamellae in polymer thin films are influenced by many factors, such as film thickness [1–5], crystallization temperature [6–10], and the interfacial interactions between the polymer and the substrate [6,8,11–14]. Monte Carlo (MC) simulations reported by Ma et al. [8] suggest that edge-on lamellae develop predominantly in thin films formed on repulsive substrates, whereas flat-on lamellae develop mainly in thin films with strong substrate interactions at high

temperatures or with particularly low film thicknesses. Wang et al. [4] observed a transition from the edge-on orientation to mainly flat-on orientations with decreasing film thickness when PE thin films are crystallized on silicon wafers (an attractive substrate), whereas for aluminum-coated silicon wafers and polyimide sheets (repulsive substrates), only edge-on lamellae are observed for all film thicknesses. Despite the importance of the interactions between polymers and substrates, most studies have been performed under conditions in which the crystallizable polymer chains strongly interact with the substrate, i.e., under wetting conditions, in an effort to avoid dewetting and to produce uniform films through spin-coating. Few experimental studies have attempted to control the substrate effects [6,13,14].

In contrast to homopolymer systems, the non-crystalline blocks in a block copolymer or the non-crystalline components in a blend can affect the surface energy at the interface between the polymer and a substrate. We have previously observed that the crystal orientation of poly(ethylene-ran-vinyl acetate) (EVA) is edge-on even in films as thin as 5 nm, and found that the vinyl acetate components of EVA affect the properties of the interface between the crystallizable ethylene component of EVA and the substrate [15]. These vinyl acetate components also affect the crystal structure. In thinner films (<20 nm), not only an orthorhombic structure

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but also a hexagonal structure is detected, and we proposed that the favorable interactions between the vinyl acetate components and the substrate might be implicated in the formation of the hexagonal structure. Hence, in this study, the crystal orientations and structures of EVA ultrathin films (5, 10 nm) spin-coated onto three different substrates (piranha-cleaned, acetone-cleaned and hexamethyldisilazane-treated Si wafers) were investigated. The interfacial properties that determine the preferred crystal orientations in the thin films are discussed in this paper. In particular, we focus on the effects of the interactions between the vinyl acetate components and the substrate on the chain conformations of the ethylene segments.

2. Experimental section

2.1. Materials and preparation

Poly(ethylene-ran-vinyl acetate) with 25 wt% vinyl acetate (EVA) was purchased from Aldrich. The weight-averaged molecular weight (M_w) and the melting point (T_m) of the sample were determined to be $150,000 \text{ g mol}^{-1}$ and $76 \text{ }^\circ\text{C}$ respectively. Three substrates were used: Si wafers cleaned in piranha solution (piranha-cleaned Si wafers), Si wafers cleaned by ultrasonication in acetone (acetone-cleaned Si wafers), and Si wafers treated with hexamethyldisilazane (HMDS-treated Si wafers). The thin films were prepared by spin-coating 0.1 and 0.25 wt% solutions of EVA in toluene. The thicknesses of the films were measured with ellipsometry (VASE, J.A. Woollam Co.). After coating, the films were kept in a desiccator at room temperature for approximately one day to induce slow solvent evaporation. The isothermally crystallized samples were first melted on a hot stage at $115 \text{ }^\circ\text{C}$ for 10 min under ambient conditions. The samples were then cooled from $115 \text{ }^\circ\text{C}$ to $60 \text{ }^\circ\text{C}$ at a rate of $5 \text{ }^\circ\text{C}/\text{min}$, then kept for 1 h.

2.2. Contact angle measurements

A 100 mm macro-lens and a digital camera (E-420, Olympus) with a six-megapixel charge-coupled device (CCD) were used. The lens was focused on the deposited droplets. Digital analysis was performed with Photoshop software to determine the contact radius R and height h at the center of each droplet. The contact angle of each droplet was calculated by using the spherical cap model and the formula $\theta = 2 \arctan(h/R)$. The surface energies of the substrates were determined from measurements for two liquids (diiodomethane and water) and by combining Young's equation and the OWK equation [16], and are shown in Table 1.

2.3. Atomic force microscopy analysis

Tapping-mode atomic force microscopy (AFM) measurements were performed with a Nanoscope IIIa/Dimension 3000 (Digital Instruments). Si tips (TESP, Veeco Instruments) with a resonance frequency of approximately 300 kHz and a spring constant of approx. 40 N m^{-1} were used. The height and phase images were collected

simultaneously. The contrast in the phase images was obtained from the phase shift of the oscillating cantilever relative to the driving signal when it interacts with the samples. The phase contrast arises essentially from differences in energy dissipation during tip-sample interaction and enables differentiation between areas with different viscoelastic properties [17]. In the phase images of crystallized polymer films, features that dissipate less energy such as crystalline phases appear brighter, whereas amorphous phases appear darker. The roughnesses of the substrates were also determined with AFM, and are shown in Table 1. The scan rate was 1 Hz s^{-1} with a scan density of 512 lines per frame.

2.4. Grazing incidence X-ray diffraction analysis

Grazing incidence X-ray diffraction (GIXRD) measurements were carried out at the 3C beamline of the Pohang Accelerator Laboratory (PAL, Korea) by using a two-dimensional (2D) CCD detector (Rayonix LLC., MarCCD-165). The synchrotron X-ray radiation had a wavelength of 1.175 \AA . The incidence angle (0.2°) was chosen to allow for complete penetration of X-rays into the polymer film. One-dimensional GIXRD profiles were extracted from the corresponding 2D GIXRD patterns.

3. Results and discussion

3.1. Surface properties of the substrates

The surface energies of the substrates were analyzed by performing contact angle measurements, and are shown in Table 1. The piranha-cleaned Si wafers have a high surface energy, whereas the HMDS-treated Si wafers have a relatively low surface energy. This trend is similar to that of the polar component. The polar component of the surface energy gradually decreases in the sequence of piranha-cleaned, acetone-cleaned, and HMDS-treated Si wafers, which indicates that the HMDS-treated Si wafers have a more hydrophobic surface than the piranha-cleaned Si wafers. The surface roughnesses of the substrates were obtained with AFM (Table 1). All three substrates have almost flat surfaces.

3.2. AFM results

Fig. 1 shows the AFM height and phase images of 10 nm films on the three substrates. In the phase images, the bright regions correspond to crystalline phases with a high modulus and the darker regions correspond to amorphous phases with a low modulus. As shown in Fig. 1a₄, b₄, and c₄, lamellar single crystals produce bright lines in the phase images. The width of a lamellar single crystal was measured by using TM-AFM and found to be approximately 10–15 nm, which indicates the formation of edge-on lamellae with the chain axis parallel to the substrate. On the piranha-cleaned (Fig. 1a) and acetone-cleaned Si wafers (Fig. 1b), the edge-on lamellae are packed along the same direction in the crystallized region, which results in bright regions in the height images. In contrast, the random packing of edge-on lamellae with no specific directionality results in dark regions in the height images. In other words, the dark regions correspond to randomly packed edge-on lamellae not to the substrate, which indicates that a polymer layer is present on the substrate. In the HMDS-treated Si wafers shown in Fig. 1c₃ and c₄, the edge-on lamellae are packed along the same direction in all regions and there are no randomly packed regions. In contrast to the other two substrates, the HMDS surface of the substrate, which produces a bright region in the phase image, is visible (white arrow). The influence of the substrate on the morphology can be more clearly seen for a 5 nm thick film (Fig. 2). As shown in Fig. 2a, the 5 nm thick film on the piranha-

Table 1
Surface energies and roughnesses of the substrates. γ_s^d and γ_s^p are the dispersive and polar components of the surface energy respectively.

	Surface energy (mJ/m^2)			Roughness (nm)
	γ_s^d	γ_s^p	γ_s^{Total}	
Piranha-cleaned	43.2	34.5	77.8	0.24
Acetone-cleaned	44.3	24.7	69.0	0.25
HMDS-treated	38.3	14.3	52.6	0.39

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