Effects of Tacticity and Crystallinity on Phase Behavior of Binary Blends Based on Polypropylenes: iPP, sPP, and aPP
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Introduction

Phase behavior of two isomeric polymers, such as poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) has been an interesting topic of studies. In the literature, the PVAc/PMA blend system is proven miscible with a stable homogeneous phase,[1,2] where PVAc differs from but is a structural isomer to poly(methyl acrylate) (PMA). On the other hands, semicrystalline polymers with the same repeat units but different tacticities (i.e., stereoisomers) are not all miscible. Phase behavior in melt state of blends of atactic polypropylenes with tactic polypropylenes (iPP, sPP, or aPP) is a difficult subject for study because the constituents all possess same chemical units with same physical properties other than different crystals at solid state. Note that the blend of two isomers, such as PVAc/PMA, differs from the blend system of two tactic polymers, such as iPP and sPP, in that the former is polar and amorphous but the latter is non-polar and semicrystalline. Blends of polystyrenes of three different tacticities (aPS, iPS, sPS) and phase or miscibility issues have also been widely studied. By contrast, iPS/sPS blends, with much lower crystallization rates and higher $T_g$’s, can be quenched to a fully amorphous state, and preserved at ambient for characterization of phase behavior of the amorphous state. It is urgent to probe and explain more thoroughly how the tacticities in crystalline packing of polymers may or may not influence the phase behavior in their amorphous state. Exactly how tacticity in polymers may influence the miscibility of blends of the polymers surely deserves a more careful investigation.

Results and Discussion

aPP/iPP blend system

Figure 1 shows plots according to the Flory-Huggins equation for determining the interaction parameter for aPP/iPP blend. The widely used Flory-Huggins equation[3]:

$$
\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R V_2}{\Delta H_f V_1} \gamma_{12} \Phi
$$

(1)
where \(1=\) aPP (amorphous), \(2=\) iPP (crystal), \(R = 1.987 \text{ (cal/mol}^\circ\text{K)}\), heat of fusion \(\Delta H_f\) for iPP = \(2.1 \times 10^3\) (cal/mol)[4], and \(V_1/V_2\) was assumed to be nearly unity = 1. The plot yielded a slope = \(2.009 \times 10^{-4}\), from which the interaction parameter was calculated to be \(\chi_{12} = -0.210\). This is a quite significant negative value, suggesting that aPP and iPP are likely miscible within range of the equilibrium melting temperatures (172\textcircled{-}190\textcircled{C}) of the blends. Whether aPP/iPP blend is also miscible below the \(T_m\) may require further clarification, which will be addressed in later sections.

**sPP/iPP blend system**

The intercepts at the \(T_m = T_m^\ast\) lines gave the equilibrium melting temperature \((T_m^\ast)\) for each of the blend compositions. Then from the \(T_m^\ast\) of each blend composition, the interaction parameter \((\beta)\) between sPP and iPP was similarly estimated from the Flory-Huggins relationship:[3]

\[
\left(1 - \frac{T_m}{T_m^\ast}\right) = -\left(\frac{R V_2}{\Delta H_f V_1}\right) \ln \phi_2 + \left(\frac{1}{n_2} - \frac{1}{n_1}\right) \phi_1 + \chi^2
\]

where \(\beta\) is the Flory-Huggins interaction parameter. Symbols of \(T_m^\ast\) and \(T_m\) are the equilibrium melting points of iPP in the polymer blends and neat crystallizable polymer (iPP), respectively. The subscript “1” indicates the non-crystallizing polymer sPP, at the chosen \(T_m\), and “2” the crystallizing polymer (iPP). \(V_1\) and \(V_2\) are the molar volumes of the repeat units of the non-crystallizing and
crystallizing polymers, and $n_1$ and $n_2$ are degrees of polymerization of these two polymer components, respectively. $\Delta H_f$ is the heat of fusion (melting) of the fully crystalline polymer (iPP) per mole repeat unit. The enthalpy of fusion for iPP has been reported to be $\Delta H_f = 2.1 \times 10^3$ cal/mol (or 8.7 kJ/mol).[4] $\Phi_1$ is the volume fraction of the non-crystallizing polymer (sPP) at selected $T_m$, which is same as the weight fraction if the density of sPP and iPP is assumed to be approximately equal (both in amorphous state). That is, $V_1/V_2 = 1$. The first two terms in the right-hand-side bracket of the above equation are due to entropic contribution to melting point depression, while the last term is enthalpic contribution to melting point depression. It can be expected that the contributions from the first two terms are small due to relatively large $n_1$ and $n_2$. For high-molecular-weight blends, the first two terms (entropic contribution) drop out and the above equation can be approximated by Eq. (1) already discussed earlier.

Table 1. Extrapolated $T_m$ (°C) for neat iPP, neat sPP and three blend systems (I. aPP/iPP, II. sPP/iPP, and III. aPP/sPP) of various compositions.

<table>
<thead>
<tr>
<th>wt/wt</th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
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<tr>
<td>0/100</td>
<td>189.85</td>
<td>189.85</td>
<td>145.18</td>
</tr>
<tr>
<td>20/80</td>
<td>184.22</td>
<td>---</td>
<td>145.17</td>
</tr>
<tr>
<td>30/70</td>
<td>183.33</td>
<td>189.79</td>
<td>145.07</td>
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</tr>
<tr>
<td>45/55</td>
<td>---</td>
<td>189.55</td>
<td>---</td>
</tr>
<tr>
<td>50/50</td>
<td>---</td>
<td>189.10</td>
<td>144.90</td>
</tr>
</tbody>
</table>

From the extrapolated values of equilibrium melting points for neat polymers (iPP) or blends of various compositions, Eq. (2) could be utilized to obtain the interaction parameter $\chi$. Figure 2 shows plot of the left-hand-side of Eq. (2) vs. $\Phi_1^2$, yielding a fairly linear line. The numerical values of $T_m^0$ or $T_m^*$ of iPP in three compositions of sPP/iPP blends are also summarized in Table 1. From these values, interaction parameter for the blend system could be estimated. The plot yielded a slope $= 2.02 \times 10^{-5}$, which led to $\chi = -0.021$, for the interaction parameter ($\chi$) between iPP and sPP in blends. This value is a small negative and can be regarded as nearly zero. For practical reason, this nearly nil value can be regarded as a slight interaction strength approaching zero, if one takes into account experimental deviations and possible uncertainty in extrapolating lamellae thickness to infinite. This nearly zero value of $\chi$ indicates that the molecular segments of sPP and iPP are less likely to be favored to form a miscible state. Although at above the melt state, the sPP and iPP molecular moiety of different configurations are comparable regardless of tacticity, at the melt equilibrium temperature at which $\chi$ is measured, the chain segments of sPP and iPP may not be fully miscible by judging from the extremely small value.
**aPP/sPP blend system**

The subscript "1" now indicates the non-crystallizing polymer aPP, at the chosen \( T_m \), and "2" the crystallizing polymer (sPP). \( V_1 \) and \( V_2 \) are the molar volumes of the repeat units of the non-crystallizing and crystallizing polymers, and \( n_1 \) and \( n_2 \) are degrees of polymerization of these two polymer components, respectively. \( \Delta H_f \) is the heat of fusion (melting) of the fully crystalline polymer (sPP) per mole repeat unit. The enthalpy of fusion for sPP has been reported to be \( \Delta H_f = 2.0 \times 10^3 \) cal/mol (or 8.3 \( \text{kJ/mol} \)).  

\( \Phi_1 \) is the volume fraction of the non-crystallizing polymer (aPS), which is same as the weight fraction if the density of aPP and sPP is assumed to be approximately equal (both in amorphous state), i.e., \( V_1/V_2 = 1 \). From the extrapolated values of equilibrium melting points for the neat polymer (iPP) or blends of various compositions, Eq. (2) could be utilized to obtain the interaction parameter \( \chi \). The numerical values of \( T_m^* \) or \( T_m^* \) of sPP in three compositions of aPP/sPP blends are also summarized in Table 1. These values were used in next-step plotting for estimation of interaction strength in this blend system. **Figure 3** shows a plot of the left-hand-side of Eq. (2) vs. \( \Phi_1^2 \), yielding a fairly linear line for the aPP/sPP blend system. The plot yielded a slope = 7.08\(^*10^{-6}\), which led to \( \Phi = -0.0071 \), the interaction
parameter (χ) between aPP and sPP in the blends, which is even smaller than that found for the sPP/iPP blend (χ = -0.0212). The values of interaction parameter for both sPP/iPP and aPP/sPP blends are essentially zero, indicating a state of free energy approaching phase separation. For practical reason, this nearly nil value can be regarded as quite slight interaction strength approaching zero, and it may represents a state of uncertain phase behavior if one takes into account some inevitable experimental deviations and possible uncertainty in extrapolating lamellae thickness to infinite. The nearly nil value of χ indicates that the molecular segments of aPP and sPP are less likely favored to form a miscible state.

**Conclusion**

Although the blends of polypropylenes have been widely studied in the past, there are still on-going debates on true phase behavior (miscibility vs. UCST). In addition, interaction strength of the blends is yet to be established. Using depression of equilibrium melting points, the Flory-Huggins interaction parameter (χ12) of the iPP/aPP blend was shown to possess a clearly negative value (-0.21), which proves and supports that the blend is indeed miscible in the melted amorphous or semicrystalline states as previously reported in the literature. However, the interaction parameters for the sPP/iPP and sPP/aPP blends were found to be nearly zero (-0.02 and -0.0071, respectively, at T_m~180°C), indicating that the interactions in these two latter blends are very weak. Experimental evidence, by OM characterization and by removing the interfering crystalline domains, revealed that upper critical solution temperature (UCST~160°C) existed in the sPP/iPP and sPP/aPP blends, which meant that they were immiscible at or below 160°C, but become miscible and homogeneous above it. The UCST in the

![Fig. 3. aPP/sPP blend plot for estimation of interaction parameter.](image-url)
blends nearly overlapped with $T_m$ of polypropylenes. This study discussed novel approaches in
discerning UCST by separating the amorphous phase domains from the crystalline spherulites.

References

   1997, 35, 1135.

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Diffraction characteristics of a liquid crystal polarization grating analyzed using the finite-difference time-domain method

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Liquid crystal polarization grating (LCPG) is a new diffraction grating formed by an interference field of two laser beams with their polarizations being orthogonal. It is interesting because most of LCPGs exhibit unique diffraction characteristics, such as polarization-independence, low scattering and high diffractive efficiency. Therefore, these devices have attracted much attention because of their great potential for various applications.

Finite-difference time-domain (FDTD) is a popular technique to model electromagnetic field distribution, since it is easy to understand, and easy to be implemented numerically. In addition, it is a time-domain method, solutions can cover a wide frequency range with a single simulation run.

In this study, a polarization grating (PG) is recorded in a LC cell (see Fig. 1). One substrate (command surface) is coated with a photosensitive azo dye-doped PVA film, whereas the other (reference surface) is a homogeneous PVA surface made by rubbing. Two coherent, orthogonally circularly polarized beams are incident onto the cell from the command substrate, and produce a polarization modulation on the command surface. The periodically modulated polarization induces periodical re-orientation of dyes via the photo-isomerization effect, which then realign the LCs in contact with the command surface, giving rise to a LCPG. A simulation that is based on the FDTD method, which accounts for the structure, demonstrates the propagation of waves in the LC grating and explains the experimental results.
The materials used herein were LC 5CB (from Merck) and azo-dyes methyl orange (MO, from Showa). Two indium-tin-oxide- (ITO-) coated glass slides, separated by two 25 μm-thick plastic spacers, are adopted to produce an empty cell. An alignment film PVA is coated onto one of the two ITO glass slides and rubbed. This surface is called the reference surface. The other is coated with an azo dye-doped PVA film, and is called the command surface. The concentration of MO doped in the PVA solution is ~ 0.75 wt %. Drops of LCs are then injected into the empty cell to produce a homogeneous sample.

Photo-induced birefringence and dichroism are associated with the trans-cis-trans photoisomerization alignment of the azo dye. The mechanism of reorientation is associated with the photoisomerization alignment of the MO azo dyes, such that their long axes are perpendicular to the polarization of the incident light after many trans-cis photoisomerization cycles. The LC molecules near the command surface are then reoriented by the dyes such that the director of the LCs is perpendicular to the polarization of the local exciting light, and the LCs close to the reference surface retain their orientation because of the strong anchoring force. Since the interference between two coherent orthogonally circularly polarized beams generates the exciting light on the command surface, the light-intensity is constant as the polarization is periodically modulated, as shown in Fig. 1. Therefore, a LCPG is fabricated.

Figures 2(a) and (b) present images observed under a POM with crossed and parallel polarizers, respectively. Notably, obvious disclination lines were present in the spacings in Fig. 2(a). The brightness in the center between the two adjacent disclination lines is low, and increases slowly toward the lines. This result is reasonable, since the LCs of the formed PG (Fig. 1) on one substrate are uni-directionally parallel to the surface, while the other substrate is rotated. The parallel alignment regions are dark, and become brighter as the twisted angle increases under cross-polarizers.
Fig. 2. Images of PG observed using a POM with (a) crossed, (b) parallel polarizers.

Figure 3(a) magnifies part of Fig. 2(a). The disclination lines are clearly observed. Figure 3(b) presents the corresponding LC director profile on the command surface. The cause of this disclination line can be understood with reference to Fig. 4. Figure 4 indicates that the twist directions from the two sides approaching the disclination line oppose each other. A disclination line must therefore exist at the boundary, consistent with the continuum theory.

Fig. 3. (a) Magnified image of PG observed under a POM with crossed polarizers, showing a sharp boundary in each grating period, (b) inferred LC directors profile on the command surface, corresponding to (a).
Fig. 4. (a) Cause of disclination lines, and (b) formed LC profile of disclination line between two periods.

An He-Ne laser is diffracted from the formed PG to investigate the diffraction characteristics. Figure 5 displays the diffraction patterns of the formed PG; (a) no polarizer (P) or analyzer (A) is placed before or after the cell, (b) with P \parallel A and (c) with P\perp A. In Fig. 5(b), the zeroth-order diffraction is bright, while weak first-order diffractions are also present. In Fig. 5(c), the zeroth-order diffraction disappears, while the first-order diffractions become bright, indicating that the polarization of the zeroth-order diffraction equals that of the incident probe beam and the first-order diffraction is elliptic.

Fig. 5. Diffraction pattern of PG (a) with no polarizer and analyzer being placed before and after the cell, (b) with P \parallel A, and (c) with P \perp A.

Figure 6(a) presents the pattern of the wave propagating in the LC cell. Figure 6(b) presents the simulated image under a crossed POM using FDTD, where the dark lines on the two sides correspond to the disclination lines. Between the two dark lines, the image exhibits a gradient in brightness. Figures 6(c) and 6(d) plot the diffraction efficiencies and the polarization states of the diffraction beams, respectively.
Fig. 6. FDTD simulated results for LCPG; (a) pattern of wave propagation in LC, where stripes represent wave-fronts, (b) simulated image of PG under crossed POM, (c) diffraction efficiency, and (d) polarization states of zeroth to fifth diffracted beams.

Figures 7(a) and 7(b) plot the measured results and the theoretically fitted results, respectively, for the zeroth- and first-order diffracted beams. Additionally, Fig. 7(a) indicates that the efficiency is maximal at an analyzer angle of 0°, and the minimum is approximately zero. This result reveals that the zeroth-order beam has the same polarization as the incident probe beam. For first-order diffraction (Fig. 7(b)), both the experimental data and the simulation reveal that the polarization is elliptic, and the long axis of the ellipse is perpendicular to the polarization of the zeroth-order beam. Figure 7(b) indicates that the experimental and simulated results are slightly mismatched. This discrepancy is associated with the slight distortion of the LC orientation in the bulk of the sample.
In conclusion, a LCPG is fabricated using photoalignment on an azo dye-doped PVA film. The FDTD approach is adopted to simulate the diffraction characteristics of the formed LCPG. The experimental results are consistent with the simulated results.

**Acknowledgements**

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A Rule Based Assembly Sequence Generation Method for Product Design
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A feasible design alternative that follows the design rules for assembly will make product manufacturing and assembly more successful. To assist designers to deal with the assembly issue in the design process, this research presents a contact relation matrix (CRM) approach to generate assembly sequences for product design. The procedure developed for the CRM approach is based on the four rules that are identified from the part contact relation and uses a matrix representation to match the recommended design alternative with the four rules. The CRM approach can be linked with an existing matrix approach in generating and evaluating design alternatives. By integrating the CRM and matrix approaches, the design quality and efficiency will be greatly improved. The CRM method is also suitable for modular assembly product sequences. A hand-held hairdryer and a coffee maker are used to demonstrate the applicability of the CRM method.

To obtain the feasible assembly sequences, product functional information and geometric relations are reviewed. There are four rules that can be used to help identify assembly sequence for each design alternative value. Based on the four rules, it is possible to identify the set of design parameter values that have contact relations with other design parameter values. Once rules for the determination of assembly sequences and contact relations between design parameter values are identified, a matching procedure can be employed to form a contact relation matrix for the generated design alternative.

The matching procedure uses a back and forth route to iteratively check for contact relations. To identify the assembly priority for the generated design alternative FDA that is based on the contact relation matrix CRM, a search procedure is developed with the array entry from the first row entries of CRM serving as a starting point. The contact relation of hand-held hairdryer design alternative is shown in Figure 1. A three-stage procedure for the CRM approach is developed followed with the identification of four rules of parts contact relations.
The research further develops a sorting procedure to generate a part assembly sequence matrix PASM. A three-stage procedure for the CRM approach is developed followed with the identification of four rules of parts contact relations. They are (1) to develop a contact relation matrix (CRM), (2) to generate an assembly priority matrix (APM) and (3) to generate a part assembly sequence matrix (PASM). The PASM reorders the design parameter values for the generated FDA. A transitional part assembly sequence matrix TPASM will be developed as a bridge to link the two matrices APM and PASM.

Once the PASM is generated as shown in Figure 2, the assembly sequence for the generated design alternative is completed. An Italian coffee maker to illustrate the modular assembly sequence is shown in Figure 3. Note that the relational database system has been used throughout the procedure development. The generation of the matrix PASM provides the information about the assembly sequence for the recommended design alternative also presents how the assembly process is made. The results show the feasibility of the CRM approach linking with the product design process.

<table>
<thead>
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<th>Recommended Design Parameter Value</th>
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<td>1. Hot Air Outlet</td>
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</tr>
<tr>
<td>2. Outlet Protect Net</td>
<td>No. 2-5</td>
</tr>
<tr>
<td>3. Handle</td>
<td>No. 3-9</td>
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<tr>
<td>4. Cold Air Inlet</td>
<td>No. 4-6</td>
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<td>5. Power Switch</td>
<td>No. 5-2</td>
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<tr>
<td>6. Handle Joint</td>
<td>No. 6-3</td>
</tr>
<tr>
<td>7. Heat Tube</td>
<td>No. 7-8</td>
</tr>
<tr>
<td>8. Motor Cover</td>
<td>No. 8-34</td>
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<tr>
<td>9. Rug</td>
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A Recommended Hand-Held Hair Dryer Design Alternative FDA

### A Portion of Contact Relations in CR

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<td>R₁ R₂</td>
</tr>
<tr>
<td>9-2</td>
<td>R₂</td>
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</tbody>
</table>

The Contact Relation Matrix CRM

Note: R₁, R₂, R₃, and R₄ denote rules of contact relations between two parts, respectively.
The designer can consider further improvement of parts appearance or integration of several parts into an individual part based on the generated assembly sequence. The CRM approach will be also connected with a matrix approach based on a congruent matrix multiplication operator, component design strategy and relational database system to the generation and evaluation of feasible design alternatives for a specific set of customer requirements. It is believed that this research effort incorporating the matrix approach will assist designers in linking customer requirements with products and corresponding assembly sequences during design development and enhance the efficiency of concurrent engineering.
Note: 1. The code in each rectangular denotes a part number.
2. The number in each circle denotes an assembly sequence.

Figure 3. Hierarchical representation of assembly sequence for coffee maker design case.
To die or not to die, that depends on the tissue environment: Tumor extracellular matrix shapes the Fas-mediated apoptosis in T cells.

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Apoptosis triggered by Fas (CD95, Apo1) receptor is one of the important ways to regulate the biological functions at cellular level. Delayed Fas-mediated apoptosis in immune cells associates with many pathological inflammatory consequences. During tumor formation, inadequate accumulation of infiltrating immune cells, mainly due to defective Fas death signaling, may play an adverse role. Pieces evidence support that tumors may high-jack accumulated infiltrating immune cells to create a tumor growth-promoting environment; this event occurs by the evasion of immune surveillance using elevated local production of IL-10, an immune-suppressive cytokines, and increased VEGF, a growth factor stimulating angiogenesis to bring in nutrition. Autoimmunity represents another pathological feature of delayed apoptosis in activated immune cells, which develops into uncontrolled inflammation. Thus, understanding the aberrant apoptosis in immune cells is an issue with therapeutic application. The mechanism conferring better viability of immune cells in the tumor tissue environment is still poorly understood. Recent knowledges about tissue environment underscore the importance of the extracellular matrix (ECM) in decisions involving the life and death of cells. By inflammation and tumorigenesis, the local status of the ECM may be profoundly perturbed. Tumors secrete various ECM components and metalloproteases in abundance, thereby altering the makeup of the immediate tissue environment.
Engagement of T cells with tumor matrix initiates PI3K/Akt pathway which suppresses the formation of DISC, stabilizes Bcl-xL and phosphorulates Bad protein at Ser 136 site. As a result, T cells in tumor tissue are insensitive to Fas-mediated apoptosis.

We undertook this question by setting up an in vitro co-culture system allowing immune cells to get into contact with a tumor cell layer mimicking the scenario in a tumor region (Su et al 2007). We evaluated the Fas-mediated apoptosis in T cells, being major effective immune cells for tumor surveillance, in this context of tumor cells contact. We found that cell-to-cell contact with tumor cells reduced Fas signal-mediated apoptosis in Jurkat T cells and activated primary human peripheral T cells. This protection ability was tumor cell line-specific. Even cells of same tumor type, such as hepatoma cell lines Huh-7 and HepG2, showed different protection abilities; the former was protective, but the latter was not. In parallel with a better viability, the apoptotic program in those tumor-protected T cells was impaired including receptor/DISC formation, mitochondrial membrane disruption, and death-executive proteases activation. Furthermore, the PI3K/Akt pathway in T cells is activated through cell-cell interaction, engagement of integrin α1β1/2 of T cells with ECM ligands of tumors, and this is essential to the prevention of apoptosis in T cells. Our findings provide a mechanistic rational to explain the accumulation of T cells within tumor tissues and highlight the role of the tumor matrix in providing PI3K/Akt survival signals for T cells and this is illustrated in the summary Figure 1 showed. Previously, we have demonstrated that tumors are able to highjack immune cells in order to create an immune suppressive environment by producing IL-10 (Yang BC, et al. 2003). The study about tumor matrix suggest that cell contact and PI3K/Akt play a key role in delaying the apoptotic program in T cells and this provides a frame work for further analysis of the tumor matrix and immune regulation.
Autoimmunity is another area that is of pathological relevance to the above findings. Local integrin-matrix interactions in inflamed tissues may provide a survival signal that leads to the expansion of the potentially autoreactive T cells that are present in the immune repertoire. If this holds true, then the integrin-matrix/PI3K/Akt pathway may be a potential target for the treatment of inflammatory disease.

References:


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Recrystallization of epitaxial GaN under indentation


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Suji Nakamura’s hard work found GaN as potential candidate for the blue light source around 365 nm for which he received the prestigious Millennium Technology Prize in 2006. Blue diode laser have the huge market for printing (1200 dpi having ~17 μm spot size with 1 mm depth of field using 6 mm optics), high density DVD memories and white light based (using diode laser based RGB) compact display devices. However, high dislocation density and related issues in GaN are one among few of the major hindrances for the application as blue laser[1]. Thus, removal of stress is one of the prime objectives for opto-electronic device applications in GaN. Growth of epitaxial (epi-) GaN film with low dislocation density either by pre-grooving the buffer layer [2] or by lateral epitaxial overgrowth (LEO) [3] is basically to reduce residual strain in the system and help crystallization process. A remarkably low threading dislocation (TD) density ~10⁷ cm⁻² is reported in epi-GaN film adopting the LEO technique. A combination of biaxial and hydrostatic stresses originating form dislocation related extended defects and point defects, respectively, are reported generally in epi-GaN.

While the above said techniques [2,3] are well reported for the growth of epi-GaN with reduced dislocation density, we have reported [4] the recrystallization of epi-GaN under indentation with various loads and loading-unloading rates. Micro-Raman spectra along with area mapping, for the spectral region of interest, are studied using 632.8 nm excitation of He-Ne laser.
Fig. 1 a) Measured values of hardness of epi-GaN(0001) with load. Loading-unloading rate is also varied for the detailed studies. b) Typical loading-unloading lines at a fixed loading-unloading rate of 10 mN.s⁻¹. The encircled regions are called as ‘pop-in’ burst.

A hardness value equivalent to bulk GaN ~10 GPa is achieved (Fig. 1a) at higher loads (> 100 GPa) or at lower loading rate (< 0.5 mN s⁻¹). This is in accordance with the conventional wisdom of materials that at low loads, where defect formation is mainly close to the surface, increasing number of extended defects (dislocations) with increasing loading rate enhances the strength (hardness) of the material. Formation of extended defects can be explained with geometrically necessary dislocation model, which in turn explains the depth dependent hardness variation for the crystalline material. Typical loading-unloading curve is shown (Fig. 1b) with ‘pop-in’ burst in the loading line (encircled). The mechanism responsible for the ‘pop-in’ burst appears to be associated with the nucleation and movement of dislocation sources including lattice atoms for the possible recrystallization process [5].
The structural transformation is studied close to the indented region using micro-Raman spectroscopy (Fig. 2). $E_2$(high) mode at 570 cm$^{-1}$ is measured outside the indented region and the value resembles the reported value of epi-GaN on sapphire substrate. Inset shows the spots measured outside and inside of the indentation mark recorded in the optical microscope attached to the spectrometer. Micro-Raman measurements inside the indented region show redshift of phonon mode gradually to 567 cm$^{-1}$ from interface region (edge of the spot) to the center of indented spot. This value is close to the calculated and measured value for $E_2$ (high) phonon of bulk GaN and its nanostructure under stress free conditions [6].

Double peaks are observed for the interface region close to the edge of the indentation (Fig. 2a), showing contributions from both the stressed outside region and stress free inside region the indented region. Raman area mapping (Fig. 2b) using spectral part of 568-573 cm$^{-1}$ shows red region lying outside the indented region and 562-568 cm$^{-1}$ shows green region lying inside the indented region. It clearly shows that the 567 cm$^{-1}$ and 570 cm$^{-1}$ peaks originates from the stress free inside region and stressed outside region of the sample, respectively. Two additional peaks at 531 cm$^{-1}$ and 559 cm$^{-1}$ (Fig. 2a) corresponding to $A_1$(TO) and $E_1$(TO) modes, respectively, are also observed in the indented region.

According to selection rule in wurtzite crystal of GaN, TO phonon modes are forbidden in the backscattering geometry for the (0001) oriented planes [6]. However, small misorientations of crystallites in the indented region allow phonon modes corresponding to other crystalline orientations.

Assuming hydrostatic stress alone inside the indentation region, a stress of <1 GPa is required for the 3 cm$^{-1}$ shift (Fig. 2a) of $E_2$(high) peak position. It is concluded from the reported [7] pressure coefficient of Raman peak of -3.55 cm$^{-1}$ GPa$^{-1}$ in GaN for hydrostatic stress alone. The distribution of pressure under the indenter given by [8]

$$p(r) = \frac{E}{2(1-v^2)} \frac{\cosh^{-1}(a/r)}{\tan \Psi}, 0 \leq r \leq a \quad \text{................................. (1)}$$

where $E$ is Young’s modulus, $v$ is Poisson’s ratio (0.22 for epi-GaN), $a$ is the contact radius, and $r$ is the radial coordinate in the surface. In the Berkovich indenter ($\Psi \sim 65.3^\circ$) with experimentally observed reduced modulus of 100 GPa, the pressure at the central region can be calculated as 10 GPa (at the boundary) to 55 GPa (exactly at the centre) using Eqn.1. Thus the estimated pressure requirement of <1 GPa for the observed Raman shift can be always provided in this technique.
Fig. 3. Micro-Raman spectra for epi-GaN outside and different regions inside the indentation spot as shown in the inset of Fig. 2a.

Fig. 4. Optical phonon modes in the wurtzite structure of GaN. Filled and unfilled symbols are represented by Ga and N, respectively. Arrows indicate directions of atomic vibrations.
Interestingly, peak ~736 cm$^{-1}$ corresponding to $A_1$(LO) mode in the different regions close to the indentation spot (Fig. 3) show no shift in peak position. A small peak ~707 cm$^{-1}$ peeps in the spectra collected from the regions inside the indentation. This peak can be assigned as surface optic mode of nanocrystalline GaN [9]. Raman scattering configuration for the wurtzite crystal of GaN(Fig. 4), for phonon corresponding to LO mode of $A_1$ symmetry is always along $Z$ direction (normal to $XY$ plane). Thus with no change in peak position of $A_1$(LO) mode, it is obvious that lattice modes normal to $XY$ plane remain unaltered. From the evolution of $E_2$(high) and TO phonon modes (Fig. 2a), collected in the backscattering geometry, it seems that stress is released in the planar direction so that Raman modes in the $XY$ plane gets modified. Thus, overall evolution of phonon modes may be due to nucleation of dislocation and release of its stress field under indentation stress to set in planar motion at the centre of indentation region by dislocation climb. Dislocation climb in the material are reported under very high hydrostatic stress due to indentation.

In conclusion, an indentation induced recrystallization is reported in epi-GaN using a Berkovich indenter. The amount of stress required for the recrystallization process is validated with the calculated value of stress in the indented volume. Dislocation stress field might have been released at the centre of indentation region with the dislocation motion under the indentation stress. A clear picture of defect dynamics, as studied in this report, will help for further understanding of the removal of dislocation in GaN leading to the possible commercialization of the material for the service of people.

References