Synthesis and Characterization of Fused Pyrrolo[3,2-d:4,5-d′]bisthiazole-Containing Polymers

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ABSTRACT
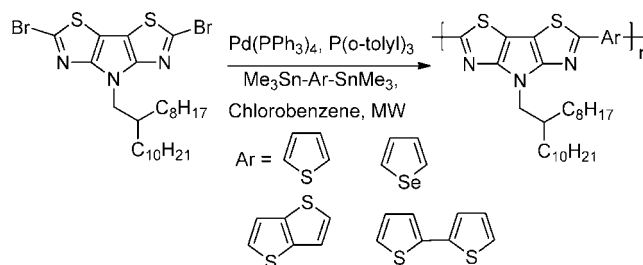
The synthesis of a novel electron-deficient fused pyrrolo[3,2-d:4,5-d′]bisthiazole is reported from 2-bromothiazole. This was copolymerized with thiophene, selenophene, thienothiophene, and bithiophene by microwave-assisted Stille polycondensation. The resulting polymers exhibited small optical band gaps combined with low-lying HOMO energy levels and demonstrated semiconducting behavior in organic field effect transistors.

The development of new π conjugated polymers has received considerable attention in the past decade, especially for applications such as organic photovoltaic cells (OPV) and field effect transistors (FETs), since they can potentially be processed in more cost-effective ways than their inorganic counterparts.[1] A promising strategy to improve the performance in FETs and OPVs has been the inclusion of fused aromatic heterocycles into the conjugated polymer backbone.

One such fused heterocycle of considerable recent interest and promise is dithieno[3,2-b:2′,3′-d]pyrrole (DTP).[2]

Several groups have reported that soluble, low band gap copolymers of N-alkylated or N-arylated DTPs show promise

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(1) (a) Arias, A. C.; MacKenzie, J. D.; McCulloch, I.; Rivnay, J.; Salleo, A. *Chem. Rev.* **2010**, *110*, 3. (b) Dennler, G.; Scharber, M. C.; Brabec, C. J. *Adv. Mater.* **2009**, *21*, 1323. (c) Chen, J.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709. (d) Pron, A.; Gawrys, P.; Zagorska, M.; Djurado, D.; Demadrille, R. *Chem. Soc. Rev.* **2010**, *39*, 2577.
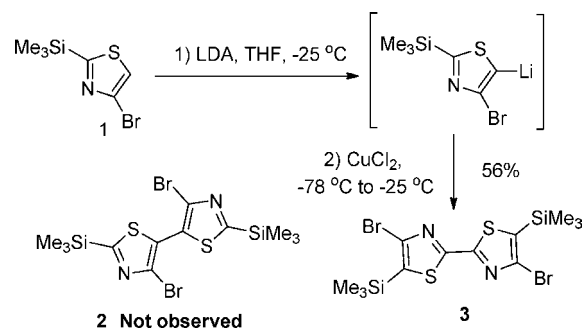
(2) (a) Berlin, A.; Pagani, G. A.; Sannicolo, F.; Schiavon, G.; Gianni, Z. *Polymer* **1991**, *32*, 1841. (b) Ogawa, K.; Rasmussen, S. C. *Macromolecules* **2006**, *39*, 1771. (c) Lu, Y.; Chen, H.; Hou, X. Y.; Hu, X. A.; Ng, S. C. *Synth. Met.* **2010**, *160*, 1438. (d) Koeckelberghs, G.; De Cremer, L.; Persoons, A.; Verbiest, T. *Macromolecules* **2007**, *40*, 4173. (e) Mishra, S. P.; Palai, A. K.; Srivastava, R.; Kamalasanan, M. N.; Patri, M. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 6514. (f) Pappenfus, T. M.; Hermanson, B. J.; Helland, T. J.; Lee, G. G. W.; Drew, S. M.; Mann, K. R.; McGee, K. A.; Rasmussen, S. C. *Org. Lett.* **2008**, *10*, 1553. (g) Vanormelingen, W.; Pandey, L.; Van der Auweraer, M.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2010**, *43*, 2157. (h) Vanormelingen, W.; Van den Bergh, K.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 5582. (i) Yassin, A.; Leriche, P.; Roncali, J. *Macromol. Rapid Commun.* **2010**, *31*, 1467. (j) Zhang, W.; Li, J.; Zhang, B.; Qin, J. G. *Macromol. Rapid Commun.* **2008**, *29*, 1603. (k) Evenson, S. J.; Rasmussen, S. C. *Org. Lett.* **2010**, *12*, 4054.

as the active components in OPV and FETs.[3] However, their device performance has been limited by the propensity for the DTP to be readily oxidized.[2k,4] In addition to limiting the ambient stability of FETs under operating conditions, the low ionization potential of DTP-containing polymers limits the available open circuit voltage available in bulk hetero-junction OPV devices, thus limiting efficiency.[5]

We were interested in developing analogues of DTP which would demonstrate improved oxidative stability, by replacement of the flanking thiophene groups with more electron-deficient thiazole groups to produce a fused pyrrolo[3,2-*d*:4,5-*d*′]-bisthiazole (PBTz). The incorporation of electron-deficient fused thiazole heterocycles, such as thiazolothiazole[6] and benzo-bisthiazole,[7] into thiophene copolymers has been reported as a promising approach to high ionization potential polymers. However, in these cases the poor solubility of both of the fused thiazole monomers necessitated the use of either high comonomer loadings,[6c] diluting the effect of the electron-deficient unit, or comonomers with bulky, branched side chains,[6b] to ensure the resulting polymers had sufficient processability in organic solvents. In contrast, PBTz contains a bridging N atom which serves as a point of attachment for a solubilizing substituent, potentially allowing copolymerization with a variety of unsubstituted comonomer units. We hereby report the synthesis of PBTz and demonstrate that it can be readily incorporated into conjugated polymer backbones.

Our initial synthetic strategy to PBTz is shown in Scheme 1 and was based upon the oxidative dimerization of commercially available 4-bromo-2-trimethylsilylthiazole **1**. However, lithiation of **1** with LDA followed by oxidative coupling with $CuCl_2$ resulted in an unexpected rearrangement to afford 4,4′-dibromo-5,5′-bis(trimethylsilyl)-2,2′-bithiazole **3** instead of the desired 4,4′-dibromo-2,2′-bis(trimethylsilyl)-2,2′-bithiazole **2** (Scheme 1).

(3) (a) Liu, J. Y.; Zhang, R.; Osaka, I.; Mishra, S.; Javier, A. E.; Smilgies, D. M.; Kowalewski, T.; McCullough, R. D. *Adv. Funct. Mater.* **2009**, *19*, 3427. (b) Steckler, T. T.; Zhang, X.; Hwang, J.; Honeyager, R.; Ohira, S.; Zhang, X. H.; Grant, A.; Ellinger, S.; Odom, S. A.; Sweat, D.; Tanner, D. B.; Rinzler, A. G.; Barlow, S.; Bredas, J. L.; Kippelen, B.; Marder, S. R.; Reynolds, J. R. *J. Am. Chem. Soc.* **2009**, *131*, 2824. (c) Price, S. C.; Stuart, A. C.; You, W. *Macromolecules* **2010**, *43*, 797. (d) Zhan, X. W.; Tan, Z. A.; Zhou, E. J.; Li, Y. F.; Misra, R.; Grant, A.; Domercq, B.; Zhang, X. H.; An, Z. S.; Zhang, X.; Barlow, S.; Kippelen, B.; Marder, S. R. *J. Mater. Chem.* **2009**, *19*, 5794. (e) Zhang, S. M.; Guo, Y. L.; Fan, H. J.; Liu, Y.; Chen, H. Y.; Yang, G. W.; Zhan, X. W.; Liu, Y. Q.; Li, Y. F.; Yang, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5498. (f) Zhang, W.; Li, J.; Zou, L.; Zhang, B.; Qin, J. G.; Lu, Z. S.; Poon, Y. F.; Chan-Park, M. B.; Li, C. M. *Macromolecules* **2008**, *41*, 8953. (g) Zhang, X.; Steckler, T. T.; Dasari, R. R.; Ohira, S.; Potscavage, W. J.; Tiwari, S. P.; Coppee, S.; Ellinger, S.; Barlow, S.; Bredas, J. L.; Kippelen, B.; Reynolds, J. R.; Marder, S. R. *J. Mater. Chem.* **2010**, *20*, 123. (h) Zhou, E. J.; Nakamura, M.; Nishizawa, T.; Zhang, Y.; Wei, Q. S.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Macromolecules* **2008**, *41*, 8302.
(4) Barlow, S.; Odom, S. A.; Lancaster, K.; Getmanenko, Y. A.; Mason, R.; Coropceanu, V.; Breídas, J.-L.; Marder, S. R. *J. Phys. Chem. B* **2010**, DOI: 10.1021/jp100774r.
(5) Scharber, M. C.; Muhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. J. *Adv. Mater.* **2006**, *18*, 789.
(6) (a) Osaka, I.; Sauve, G.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *Adv. Mater.* **2007**, *19*, 4160. (b) Osaka, I.; Zhang, R.; Liu, J. Y.; Smilgies, D. M.; Kowalewski, T.; McCullough, R. D. *Chem. Mater.* **2010**, *22*, 4191. (c) Osaka, I.; Zhang, R.; Sauve, G.; Smilgies, D. M.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2009**, *131*, 2521.
(7) (a) Ahmed, E.; Kim, F. S.; Xin, H.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 8615. (b) Osaka, I.; Takimiya, K.; McCullough, R. D. *Adv. Mater.* **2010**, DOI: 10.1002/adma.201002117.
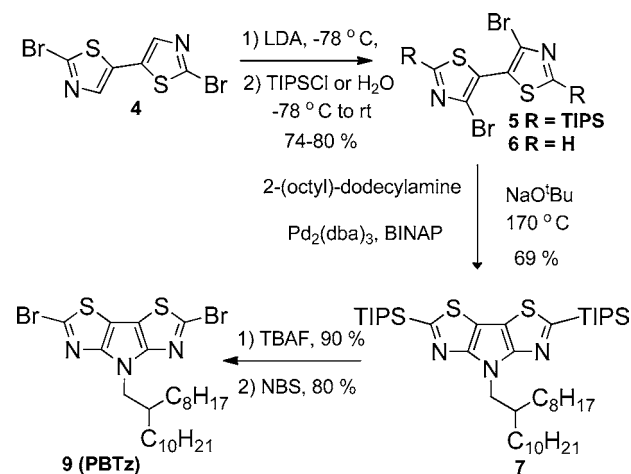
Scheme 1. Unexpected Rearrangement During Lithiation

The structure of **3** was confirmed by single-crystal X-ray analysis (Figure S1, Supporting Information). Zambon et al. recently reported similar migrations of trimethylstannyl and trimethylsilyl groups in thiazole systems,[8] and in analogy to their work we propose that the initially formed 5-thiazole anion reacts in an intramolecular fashion by nucleophilic attack on the trimethylsilyl group, which generates the more thermodynamically stable 2-thiazole anion. This then oxidatively dimerizes upon treatment with $CuCl_2$ to afford **3**. We note that Getmanenko and Marder recently reported that replacement of the TMS group with the more sterically bulky tri(isopropyl)silyl (TIPS) group suppressed silyl migration under similar reaction conditions.[9]

Due to the high expense of **1**, we therefore developed an alternative route based upon readily available 2-bromothiazole (Scheme 2). As reported by Knochel, reaction with

Scheme 2. Synthesis of Pyrrolo[3,2-*d*:4,5-*d*′]bisthiazole (PBTz)

$(tmp)_2Zn·2MgCl_2·2LiCl$ (tmp = 2,2,6,6-tetramethylpiperidine), followed by oxidation of the resulting diarylzinc

(8) Zambon, A.; Borsato, G.; Brussolo, S.; Frascella, P.; Lucchini, V. *Tetrahedron Lett.* **2008**, *49*, 66.
(9) Getmanenko, Y. A.; Tongwa, P.; Timofeeva, T. V.; Marder, S. R. *Org. Lett.* **2010**, *12*, 2136.

compound with chloranil, afforded 2,2′-dibromo-5,5′-bithiazole **4** in good yield without any competing rearrangement products.[10] Now taking advantage of the fact that β-lithiated thiazoles readily rearrange to the more thermodynamically stable α position by the base-catalyzed halogen dance mechanism,[11] we observed that treatment of **4** with 2 equiv of LDA, followed by quenching with either tri(isopropyl)-chloride (TIPSCl) or water, afforded **5** or **6** in yields of 74% and 80%, respectively.

The structures were confirmed by single-crystal X-ray, which demonstrates both molecules pack in the transoid configuration. Our structure of **5** matches that recently published.[9] Interestingly, we observe significant differences between the crystal structures of **5** and **6**, especially with regard to the torsion angle between the two thiazole rings which is 45.45° for **6**, but only 0.44° for **5**. In addition, compound **6** crystallizes into a columnar arrangement in which four molecules of **6** form a cyclic tetramer (Figure 1). These rings are characterized by an intermolecular H
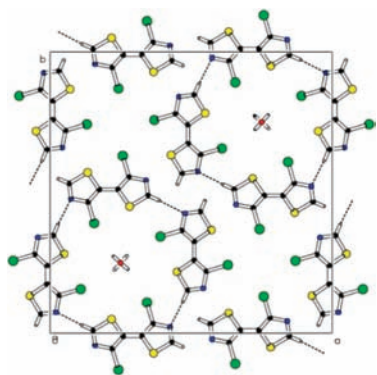
**Figure 1.** Crystal structure images of compound **7** showing intramolecular interactions.

bonding interaction between H(1) of one dimer and N(2) of an adjacent dimer [C(1)H(1)N(2) bond angle 168.85°, H(1)···N(2) 2.444 Å, which is significantly shorter than the sum of the van der Waals radii 2.75 Å]. The tetramers stack on top of one another to form a columnar structure with a central void of 3.82 Å, which is filled by a water molecule. In contrast, any possible H-bonding is suppressed in **5** by the attachment of the silyl group, and the molecule is characterized by intramolecular noncovalent interactions between the S and Br atoms, in addition to intermolecular Br···Br contacts.[9]

PBTz **9** was synthesized via a Buchwald–Hartwig coupling between silylated bromide **5** and a branched alkyl amine in 69% yield.[12] Branched amines were chosen to ensure solubility of the resulting polymers. We found that

higher yields were obtained by heating in a sealed tube at 170 °C, with mainly the monoaminated product obtained in refluxing toluene. Subsequent deprotection using TBAF afforded compound **8**, which was directly brominated with NBS in DMF to afford **9** in a combined yield of 71% from **5**. Attempts to synthesize compound **8** directly from **6** under the same reaction conditions resulted in a complex mixture in which the dibromide **6** was fully consumed, but no desired product could be detected by GCMS or NMR. This may be due to competing direct Pd-catalyzed arylation reactions at the 2-positions of the thiazole ring. Similar reactions have been observed in the presence of Pd, aryl bromides, and base.[13]

Compound **9** was copolymerized with the respective bis(trimethylstannyl) monomers of thiophene, bithiophene, thieno[3,2-b]thiophene, and selenophene by microwave-assisted Stille polycondensation[14] (Scheme 3), to afford

Scheme 3. Synthetic Route for the Preparation of Polymers PTzT, PTzBT, PTzTT, and PTzSe
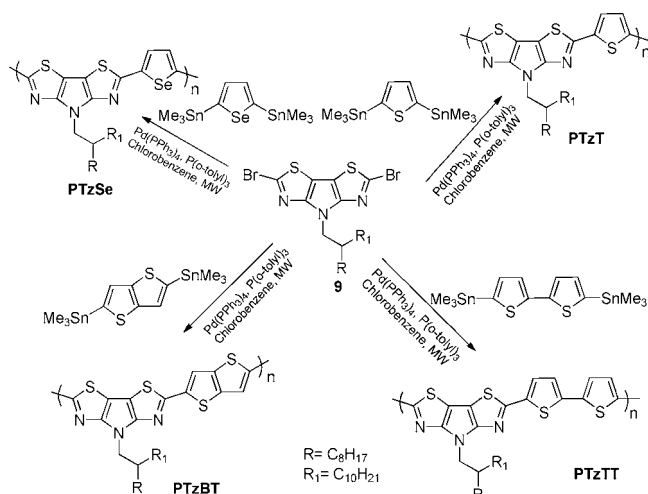
PTzT, PTzBT, PTzTT, and PTzSe, respectively, in good yields. Initial attempts involving Stille cross coupling between **9** and bis(trimethylstannyl) thiophene using Pd$_2$dba$_3$/P(o-tol)$_3$ as the catalyst system afforded relatively low molecular weight products, and modifying the catalyst to Pd(PPh$_3$)$_4$ resulted in higher molecular weight polymers.

All polymers were purified by Soxhlet extraction with methanol, acetone, and hexane to remove catalyst residues and low weight oligomers, followed by precipitation of a chloroform solution of the polymer into methanol. The resulting polymers were all soluble in common organic solvents such as THF, toluene, chloroform, and chlorobenzene at room temperature and readily formed uniform dark blue films by either spin coating or drop casting at room temperature.

(10) Wunderlich, S. H.; Knochel, P. *Angew. Chem.* **2007**, *46*, 7685.

(11) (a) Stangeland, E. L.; Sammakia, T. *J. Org. Chem.* **2004**, *69*, 2381. (b) Stanetty, P.; Schnurch, M.; Mereiter, K.; Mihovilovic, M. D. *J. Org. Chem.* **2005**, *70*, 567.

(12) Koeckelberghs, G.; De Cremer, L.; Vanormelingen, W.; Dehaen, W.; Verbiest, T.; Persoons, A.; Samyn, C. *Tetrahedron* **2005**, *61*, 687.

(13) (a) Liegault, B.; Lapointe, D.; Caron, L.; Vlassova, A.; Fagnou, K. *J. Org. Chem.* **2009**, *74*, 1826. (b) Yokooji, A.; Okazawa, T.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2003**, *59*, 5685.

(14) Tierney, S.; Heeney, M.; McCulloch, I. *Synth. Met.* **2005**, *148*, 195.

Table 1. Optical and Electrochemical Properties of the Polymers PTzT, PTzBT, PTzTT, and PTzSe

polymer	M_w (g/mol)	M_n (g/mol)	PDI	λ_{max} (CHCl$_3$, nm)	λ_{max} (film, nm)[a]	λ_{onset} (film, nm)	E_g^{opt} (film, eV)[b]	HOMO[c] (eV)	LUMO[d] (eV)
PTzSe	32000	24000	1.3	632	645, 725 (sh)	795	1.56	−5.25	−3.69
PTzT	29000	15000	1.5	616	627	760	1.63	−5.30	−3.67
PTzTT	33000	23000	1.4	566	573	750	1.65	−5.20	−3.55
PTzBT[c]	74000	43000	1.7	577	613, 675 (sh)	725	1.71	−5.15	−3.45

[a] Drop cast from chloroform solution, shoulder (sh). [b] Band gap estimated from λ_{onset} $E_g^{opt} = 1240/\lambda_{onset}$. [c] HOMO levels measured by photoelectron spectroscopy in air. [d] LUMO levels of the polymers were obtained from the equation LUMO = HOMO + E_g^{opt}.

The polymers all exhibited good molecular weights as determined by GPC, with M_w in the range of 29−74 KDa (Table 1). The optical properties of the polymers were measured in solution at room temperature and at 100 °C, as well as in thin films prepared by drop casting. The spectra are shown in Figure S3 (Supporting Information) and the data summarized in Table 1. All polymers exhibited relatively broad absorption at room temperature in chloroform solution, with absorption maxima in both solution and solid state that are significantly red-shifted compared to thiophene homopolymers like P3HT,[15] which we attribute to the presence of the rigid PBTz unit in the polymer backbone, leading to a more planar polymer backbone with enhanced delocalization. In addition, PBTzBT exhibits a significant red shift compared to the DTP bithiophene polymer, which absorbs at 492 and 527 nm in solution and thin film, respectively.[16]

The drop cast films exhibited a small red shift in λ_{max} of between 7 and 36 nm compared to the solution spectra, suggesting the polymers may already be in an extended chain conformation in solution, similar to that observed for DTP polymers.[2b] Longer wavelength vibronic shoulders were observed for PTzTT and PTzSe, suggesting interchain delocalization in the solid state. PTzTT and PTzSe also exhibited signs of aggregation in room-temperature solutions, with longer wavelength shoulders appearing in the spectra. The intensity of these shoulders was reduced by heating the solutions. In agreement with previous observations, the selenophene copolymer exhibited the lowest band gap due to the stabilizing effect of selenophene on the polymer LUMO.[17] The HOMO energy levels were estimated by measuring the ionization potential of a thin film in air using the PESA technique,[18] confirming the relatively low-lying HOMO energy levels.

The charge transport properties of the polymers were investigated in transistor devices. Devices were fabricated onto bottom gate, bottom contact (Au) devices using heavily doped Si++ substrates as the gate electrode and a 200 nm thermally oxidized SiO$_2$ layer as the gate dielectric. The SiO$_2$ layer was treated with the primer hexamethyldisilazane (HMDS) to passivate the surface. Polymers were then deposited by spin coating and dried at 120 °C for 30 min before measurement. The results are summarized in Table 2. Only p-type transport was observed, with modest charge

Table 2. Charge Carrier Mobilities (μ) and Current On/Off Ratios (I_{on}:I_{off}) of the Polymers

polymer	$I_{on/off}$	μ_{lin} cm^2 v^{-1} s^{-1}	μ_{sat} cm^2 v^{-1} s^{-1}
PTzSe	10^4	4.8 × 10^{-5}	5.5 × 10^{-5}
PTzT	10^4	2.20 × 10^{-5}	7.5 × 10^{-5}
PTzTT	10^4	5.6 × 10^{-5}	6.7 × 10^{-5}
PTzBT	10^5	1.5 × 10^{-4}	1.1 × 10^{-3}

carrier mobilities. The transfer and output plots for the best performing polymer PTzTT are shown in Figure S2 (Supporting Information). They demonstrate negligible hysteresis between the forward and reverse transfer sweeps, with no significant evidence of contact resistance in the output characteristics at low drain voltages. The relatively low charge carrier mobilities observed could be related to the bulky side chains used in this study, which may suppress close packing of the polymer backbones; nevertheless, they should be sufficient for photovoltaic applications.

In conclusion, we have developed a route to novel dithiazolopyrrole monomers and incorporated them in donor−acceptor copolymers. The resulting polymers demonstrate high ionization potential, low band gap, and good solubility in most common organic solvents and show promise for use in optoelectronic devices. Further investigations into their photovoltaic performance are ongoing.

Supporting Information Available: Detailed experimental procedures and full characterization data for **3−9**. Crystal data and full crystallographic information for **3** and **6** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) McCulloch, I.; Bailey, C.; Giles, M.; Heeney, M.; Love, I.; Shkunov, M.; Sparrowe, D.; Tierney, S. *Chem. Mater.* **2005**, *17*, 1381.
(16) Liu, J. Y.; Zhang, R.; Sauve, G.; Kowalewski, T.; McCullough, R. D. *J. Am. Chem. Soc.* **2008**, *130*, 13167.
(17) (a) Heeney, M.; Zhang, W.; Crouch, D. J.; Chabinyc, M. L.; Gordeyev, S.; Hamilton, R.; Higgins, S. J.; McCulloch, I.; Skabara, P. J.; Sparrowe, D.; Tierney, S. *Chem. Commun.* **2007**, 5061. (b) Zade, S. S.; Zamoshchik, N.; Bendikov, M. *Chem.—Eur. J.* **2009**, *15*, 8613. (c) Patra, A.; Bendikov, M. *J. Mater. Chem.* **2010**, *20*, 422.
(18) Uda, M. J. *J. Appl. Phys.* **1985**, *24*, 284.