

Printing Approaches for Large-Area Color Organic LED Displays

J.C. Sturm, F. Pschenitzka, T.R. Hebner, M.H. Lu, and S. Troian*
Center for Photonics and Optoelectronic Materials (POEM)
Department of Electrical Engineering, *Department of Chemical Engineering
J-301 E-Quad, Olden St.
Princeton University, Princeton, NJ 08544 USA
609-258-5610 fax: 609-258-1954
sturm@ee.princeton.edu

ABSTRACT

In this paper the fundamental properties underlying the transfer of organic fluorescent dyes to local areas in polymer thin films by both liquid phase (ink-jet printing) and evaporation/diffusion transport methods are examined, with the goal of achieving full color displays based on organic light emitting diodes made from such polymers. Ink-jet printing offers a simple non-contact method for forming patterns, but a critical issue is the redistribution of dyes and other molecules in the liquid droplet before it dries. Masked large area evaporations allows one to rapidly pattern large areas, but its rate depends on the ability of dyes to diffuse through polymer films.

Keywords: Ink-jet printing, organic light emitting diode, organic electroluminescence, diffusion, flat panel display, color integration

INTRODUCTION

A critical technological issue in the area of organic light emitting diodes is a method to achieve full color integration. Specifically, one must integrate red, green, and blue-emitting devices onto a common substrate in a patterned fashion, along with providing electrical contacts to each device. The most energy efficient approach is probably to integrate different organic layers for each color, as opposed to fabricating white devices combined with patterned color filters. Among the methods reported for integrating color devices are moving a shadow mask *in situ* for the evaporation of small molecule devices [1,2], etching blanket organic layers using evaporated metal or photoresist masks [3,4], ink-jet printing of complete polymer layers themselves [5,6], or stacking the three different devices on top of each other [7]. Moving a shadow mask with a resolution on the scale of microns (for small pixels) *in situ* in close proximity to the sample is technologically challenging. The method of etching blanket organic layers is difficult because of the difficulty of obtaining a small metal or photoresist etch mask in practice without damaging the organic layer. When ink-jet printing complete polymer layers, it might be difficult to precisely control the shape of the final polymer layer. Independently contacting the different layers in the stacked structure might be problematic.

An alternative for integrating three-color devices is just to add the a dye which changes the emission color to a previously formed planar organic layer [8,9]. This has been demonstrated by both ink-jet printing (or dye-droplet application) and large-area diffusion [10]. The first method transfers dye in the liquid phase and the second transfers dye in the vapor phase. With both of these methods, the final lateral and vertical profile of the dye in the final polymer film is a critical issue. The profiles of such dyes and the mechanisms on which they depend are addressed in this paper.

MASS TRANSPORT ISSUES IN LOCALIZED LIQUID PHASE PROCESSES

Once one has a uniform polymer layer (prepared by spin-coating, e.g.), one can locally add a dye which changes the emission color of the polymer layer by locally applying a dye in a liquid droplet (by ink-jet printing, e.g.) to the surface of the polymer film (Fig. 1(a)). In our first work, the polymer was polyvinylcarbazole (PVK) and the dye was Coumarin 6 (C6) dissolved in acetone, which does not dissolve the PVK layer. After the droplet was applied to the surface and it dried, the electroluminescence (EL) and photoluminescence (PL) color of the film changed in the region which was in contact with the droplet from the deep blue of the host to the green of the dye [8]. In the case of the acetone/PVK system, it was previously found that the vertical distribution of the dye throughout the PVK was already uniform after the drying of the acetone at room temperature (Fig. 1 (b)). Presumably some amount of acetone was absorbed by the PVK to lower its glass transition temperature, so the C6 could rapidly diffuse throughout the film [8]. In this paper we examine the lateral distribution of the dye across the spot.

We initially expected a higher level of dye in the center of the spot, assuming that the droplet would shrink uniformly in size while drying, so that the center was exposed to dye-containing solution for a longer time than the edge. However, the UV fluorescence from the dye was clearly stronger near the edge of the spot than in the center, with a distinct "ring" noticeable at the edge. Fig. 2 shows the case when an 11 microliter droplet of C6 dissolved in acetone (0.3 mg/ml) was applied. Qualitatively similar phenomena appeared in much smaller droplets as well. An X-ray microprobe tuned for sulfur, which was present only in the C6 dye and not in the PVK, confirmed a higher concentration of dye at the edge of the spot than at the center. To understand this phenomenon, in contrast to what was initially expected, one must realize that the droplet is being applied to an essentially impermeable surface (the ITO/glass), since the PVK thickness is small compared to the height of the droplet on the surface (100's of microns). Therefore lateral redistribution of dye in the liquid phase will dominate over lateral distribution in the polymer itself, and the final dye concentration (and PL) in the polymer is to first order just a marker of where the dye was left after it redistributed in the liquid phase.

The lateral redistribution of solute or small particles in a colloidal suspension during the drying of droplets on hard surfaces has been extensively studied, although the results are still not well understood [11-15]. Two phenomena are required for the redistribution of the solute or particles to the edge of the droplet, resulting in a "coffee-stain" type of effect. The first is the mass transport of the liquid in the droplet during the

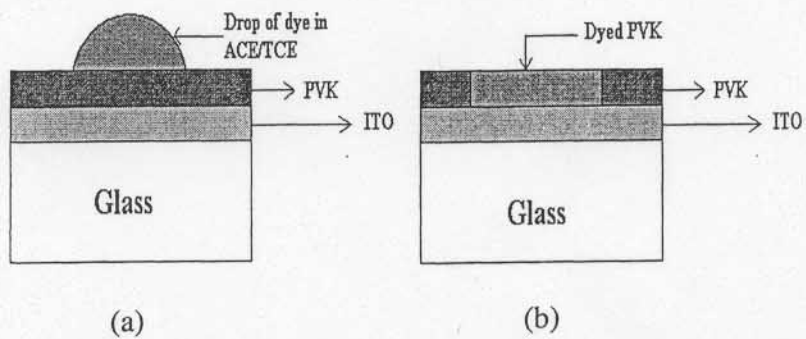


Fig. 1. Method of dye printing onto planar organic film showing vertical diffusion of dopant into film as solvent dries to change its emission properties.

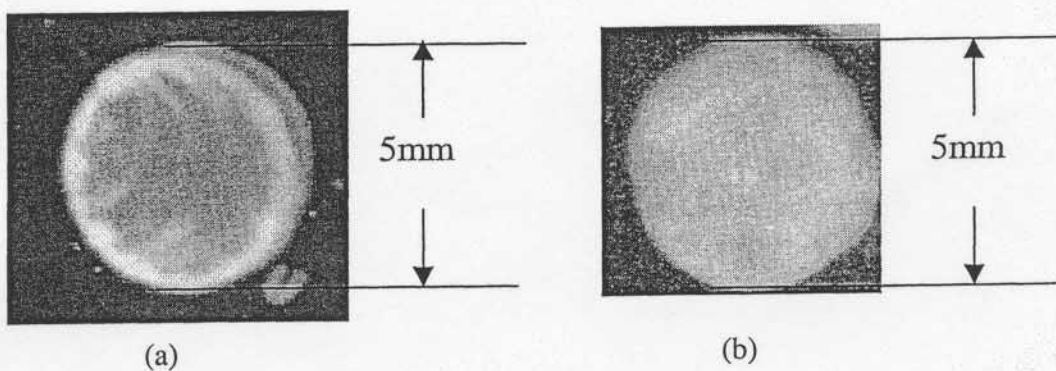


Fig. 2. UV fluorescence image of PVK film after drying of C6/acetone droplet (a) at room temperature and (b) 4 °C.

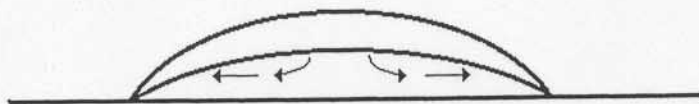


Fig. 3. Schematic cross section of droplet drying during with edge pinning and differential edge evaporation, leading to mass transport to the edge of the droplet.

drying. There are two main reasons for the mass transport of the liquid. The first is the relatively higher evaporation rate of the solvent at the edge of the drop than near its center, either due to vapor pressure effects or thermal effects. Second, the thermal gradients within the drop as it dries can lead to very complex thermally-driven convective recirculating flow patterns within the droplet, often referred to as Marangoni-driven flows. They can be especially severe with acetone [14-15]. The second criteria needed for "ring" effects is "edge-pinning" of the droplet diameter as it dries. This means that the contact angle of the droplet does not stay fixed, but rather the edge of the droplet stays pinned as the droplet evaporates. If edge pinning is combined with evaporation which preferentially takes place at the edge of the dot, then there must be transport of the fluid (and dye) from the center of the droplet towards the edge (Fig. 3).

The lateral size of the droplet (11 microliter initial volume) as a function of time after it was applied is shown in Fig. 4. Note that indeed it is constant for most of the total drying time of 50 seconds. Further, note that the final dye profile shows evidence of several further "stick/slip" cycles occurring after the droplet diameter finally did begin to shrink in size. To reduce the severity of this effect, we then reduced the overall rate of evaporation by cooling the substrate to 4 °C. A slower evaporation rate reduces the driving forces for the flow of dye to the edge of the droplet. In this case the pinning time increased slightly to 60 sec, but the total evaporation time was increased by a factor of five to 250 sec. With a slower evaporation rate, a more uniform dye profile, as observed by UV fluorescence, was indeed observed (Fig. 2(b)).

In single-organic-layer devices made with PVK, we have previously added the small molecule PBD to the polymer solution (chloroform-based) to create a doped polymer layer after spin-coating. The PBD increases the film electron mobility and decreases the device turn-on voltage [16]. However, using such films with the dye doping technique (with acetone) was not successful. The acetone dissolved the PBD from the doped film before it dried, and the PBD was subject to the same redistribution effects as the dye which was added with the acetone. When the initial weight ratio of the PVK:PBD was 100:40, after the acetone droplet dried the thickness of the film inside the spot where the acetone was applied was reduced from ~130 to ~100 nm (Fig. 5(a)). No such redistribution was evident when no PBD was in the film. (The points in Fig. 5 were taken at individual locations by interferometry. At the very edge of the spot, it could clearly be seen that excess material (presumably PBD) had piled up, but no interferometry was possible because of the rough surface at the edge.)

To prevent the redistribution of the electron transport groups, we then synthesized a random co-polymer which contained both carbazole and oxadiazole side groups for hole and electron transport, respectively [17] (Fig. 6). The EL and PL colors of these films could easily be changed by acetone droplets containing C47 (blue), C6 (green) and Nile red as described above. In this case however, because the oxadiazole groups were covalently bonded to the polymer backbone and could not be dissolved by the acetone, which would lead to lateral redistribution, no change in the film thickness was observed (Fig. 5(b)). Using a copolymer film with a thickness of 135 nm and carbazole/oxadiazole

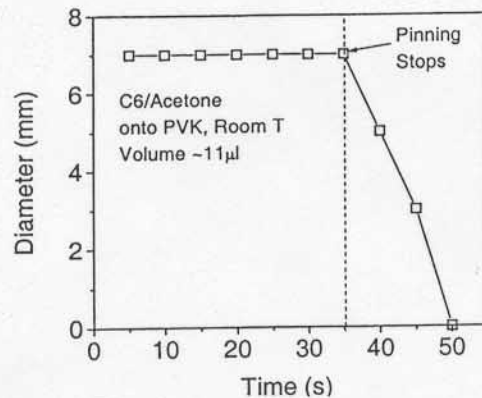
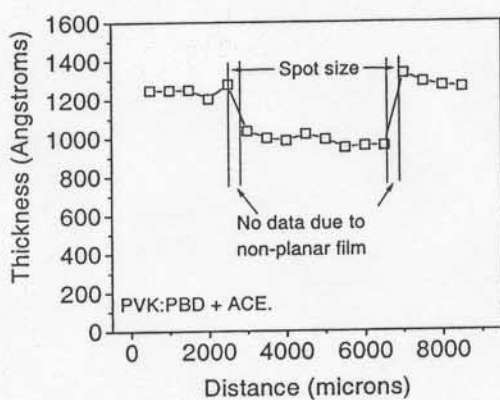
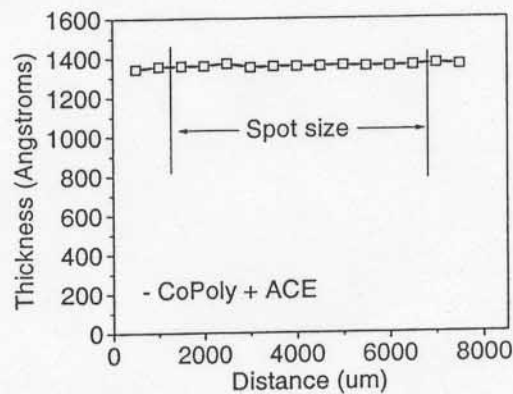


Fig. 4. Liquid spot size vs time after an 11-microliter dye/acetone droplet was applied to a PVK film at room temperature.



(a)



(b)

Fig. 5. Thickness by interferometry after an acetone drop was applied to a PVK:PBD (100:40 by weight) film and (b) to a copolymer film with PVK and oxadiazole groups.

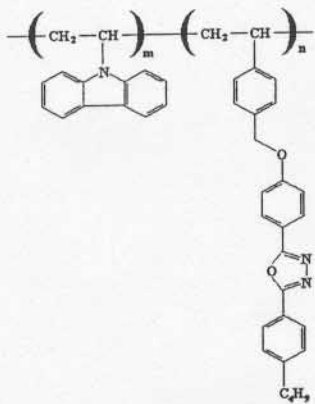


Fig. 6. Schematic diagram of random copolymer with carbazole and oxadiazole side groups [17].

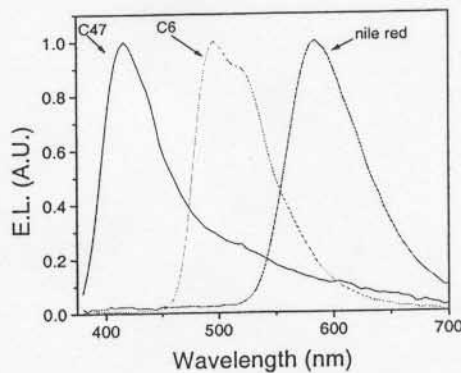


Fig. 7. EL spectra of copolymer of Fig. 6 locally doped by wet printing with C47, C6, or Nile Red to integrate RGB devices.

mole ratio of 83:17, red, green, and blue emitters could be integrated into a single copolymer film by doping through dye droplets (Fig. 7).

DYE TRANSFER BY LARGE AREA DIFFUSION

To entirely avoid the issues associated with liquid phase transport of dopants during drying, we have also locally introduced dopants using a dry process [10] (Fig. 8). In this process, dye is thermally diffused locally into the polymer through a mask. Unlike conventional evaporation through a shadow mask, in this process a large-area source is used, and the source plate, mask, and target polymer film are all sandwiched together during the heating cycle. The process has been successfully carried out in both air and vacuum. In our early work, the source plate was formed by the conventional evaporation of dopant onto a piece of glass. This had the drawback that the subsequent transfer of dye from the source to the target was difficult to control, and that vacuum was required for forming the source plate. Therefore the source plate is now formed by spin-coating a polymer (e.g. PVK) which is very heavily doped with dye in solution before deposition.

We previously have shown that as the sandwich of Fig. 8 is heated (in the temperature range of 50 – 100 °C, the photoluminescence from the dye in the target film increases sharply to dominate the spectrum [10]. While some remnant of the PVK emission is still evident in the PL spectra, EL spectra show only emission from the dye, possibly due to a different excitation mechanism between EL and PL in this material system [16]. Further, if two dyes are present, PL shows emission from both dyes, whereas EL shows emission from only the lower-energy dye. This allowed us to demonstrate a pixellated RGB emitter with only two patterned diffusion steps (C6 and Nile Red) by starting with a spin-coated film already doped with bimeane (blue) [18]. A minimum lateral resolution of 160 microns was demonstrated in initial experiments, but needs further work. In the rest of this paper, we focus on the vertical dye profile in the target film.

Our goal was to study the rate of incorporation and profile of the C6 into the film. To track the motion of the dye into the target film, we first characterized the PL ratios from bimeane and C6 in films uniformly containing both dyes in different proportions (created by spin-coating). A film was then spin-coated with a known uniform level of bimeane only, and C6 (or Nile red) was added to the film by the large-area diffusion method. First, Fig. 9 shows the C6/bimeane PL ratio (roughly proportional to the amount of C6) in the top of the PVK film as a function of diffusion temperature for a 30 min. transfer cycle. Note the process is strongly dependent on temperature, with the C6 signal changing nearly 100 X as the transfer temperature was changed from 50 to 80 °C. To learn more about the dye profile, we performed the experiments on sapphire substrates which are transparent to both the visible PL signal as well as to the UV pump. Thus we could perform PL either from the top or bottom of the PVK films. Because the absorption length of the UV pump (50 nm at the wavelength of 254 nm) in the PVK host is much less than the film thickness (~100 nm), by comparing top and bottom incidence

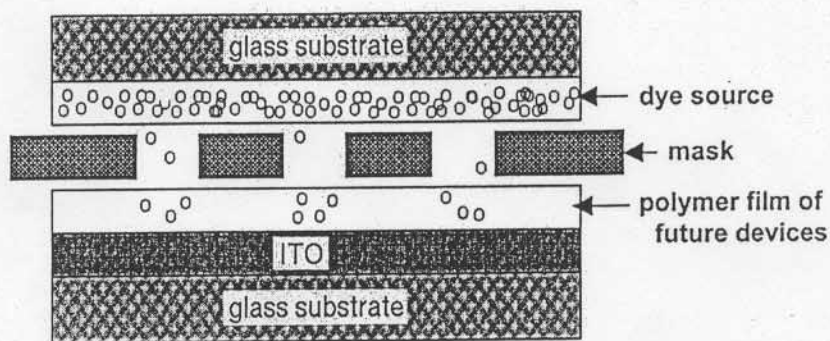


Fig. 8. Schematic diagram of large-area masked diffusion process [10].

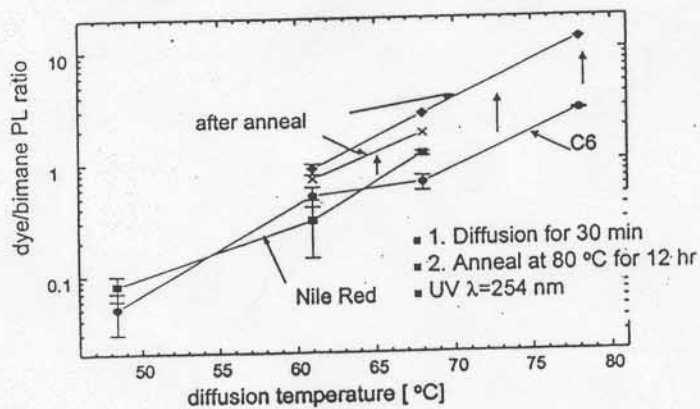


Fig. 9. Dye/bimane PL ratio after a 30 min. transfer step as function of the transfer step temperatur, both after the initial step and after a further 12-hr 80 °C anneal with the dopant source removed. For C6 and Nile red into PVK.

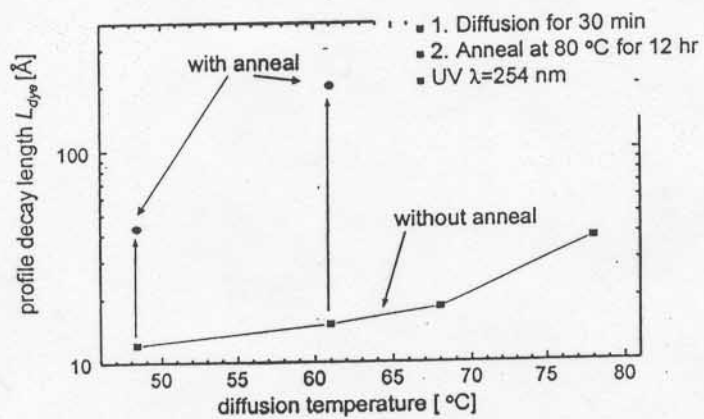


Fig. 10. Estimated profile decay length after intial 30 min initial transfer step (as a function of its temperature) and after a further 12-hr 80 °C anneal. (C6 in PVK).

PL measurements, we can get an estimate of the relative depth to which the dye has diffused.

Although the exact shape of the diffused profile was not known, and one could justify several kinds of profiles theoretically, for simplicity we assumed the dye decay profile a simple exponential decay, with a decay length of L_{dye} . Fitting this profile to the observed data from top and bottom PL (and accounting for the finite absorption length of the pump), the dye decay length after the initial annealing step was extracted (Fig. 10). Note that the decay length was very short (a few nm), implying a relatively sharp decay in the dye profile through the film. To flatten the dye profile, the sample was then further annealed for 12 hrs at 80 °C with the dye source removed. The total amount of dye emission then increased (Fig. 9), suggesting that after the initial dye transfer step that some dye which was inactive in PL had piled up on the sample surface (or was just inside the sample and was inactive in PL for other reasons). The diffusion step then drove the dye further into the PVK where it became active. Second, the dye decay length increased sharply (Fig. 10), rising a few nm to 20 nm for a diffusion initially performed at 60 °C. For diffusions performed at 68 °C or more, the profiles were essentially flat throughout the film after annealing. Note that such flat profiles in this case required high temperature annealing to distribute the dopant uniformly throughout the film. This is in contrast to the case when the dopant is applied through wet solvent droplets as described above, in which case the dye (for appropriate choice of materials and solvents) is uniformly vertically distributed immediately after the droplet dries. Further work is needed to extract exact dye diffusion coefficients as a function of temperature.

CONCLUSIONS

The local of doping of polymers by dyes to change emission color is an attractive path for the formation of integrated red, green, and blue organic light emitting devices for display applications. If the dye is applied by a liquid method, such as in ink-jet printing, a critical issue is the lateral distribution of dye during the droplet drying process. If the dye is applied via a dry process both the lateral and vertical profiles are of interest, with dye diffusion controlling the vertical profile. Both methods are extremely promising and have been used to demonstrate the integration of red, green, and blue LED's.

ACKNOWLEDGEMENTS

This work was supported by DARPA and NSF. The collaboration of R. Register and X. Jiang (Princeton) and M. Thompson (USC) on copolymer synthesis is acknowledged.

REFERENCES

1. S. Miyaguchi, S. Ishizuka, T. Wakimoto, et al., Ext. Abs. Fourth. Int. Conf. Sci. Tech. Display Phosphors, Bend, Oregon, (1998).
2. Y. Iketsu, E. Kitazume, T. Tanaka, E. Nishigaki, S. Ootsuki, and K. Mizoguchi, Proc. SPIE **3476**, 226-231 (1998).
3. C.C. Wu, J.C. Sturm, R.A. Register and M.E. Thompson, Applied Physics Letters **69**, 3117-3119, (1996).
4. D.G. Lidzey, M.A. Pate, M.S. Weaver, T.A. Fisher, D.D.C. Bradley, Synthetic Metals **82**, 141-148, (1996)
5. T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu and J.C. Sturm, Appl. Phys. Lett. **72**, 519-521, (1998).
6. T. Shimoda, S. Kanbe, H. Kobayashi, S. Seki, H. Kiguchi, et al, SID 99 Digest, 376-379 (1999).
7. P.E. Burrows, S.R. Forrest, S.P. Sibley and M.E. Thompson, Applied Physics Letters **69**, 2959 (1996)
8. T.R. Hebner, J.C. Sturm Appl. Phys. Lett. **73**, 1775-1777 (1998).
9. S-C. Chang, J. Bharathan, Y. Yang, R. Helgeson, F. Wudl, M. B. Ramey, and J. R. Reynolds, Appl. Phys. Lett, **73**, 2561-2563 (1998).
10. F. Pschenitzka and J.C. Sturm, Appl. Phys. Lett **74**, 1913-1915 (1999).
11. R. D. Deegen, O. Bakajin, T.F. Dupont, G. Huber, S.R. Nagel, and T.A. Witten, *Nature* **389**, 827-829, 23 Oct. (1997).
12. J. Conwat, H. Korn, and M.R. Fisch., *Langmuir* **13**, 426-431, (1997).
13. E. Adachi, A.S. Dimitrov, and K. Nagayama, *Langmuir* **11**, 1057-1060, (1995).
14. N. Zhang and W.J. Yang, J. Heat Transfe, **104**, 656-662 (1982).
15. N. Zhang and W.J. Yang, Experiments in Fluids **1**, 101-111 (1983).
16. C.C Wu, J.C. Sturm, R.A. Register, J. Tang, L. Dana, M.E. Thompson, *IEEE Transactions on Electron Devices* **44**, 1269-1281, (1997).
17. X. Jiang, R.A. Register, F. Pschenitzka, J.C. Sturm, K.A. Killeen, M.E. Thompson, Spring Meeting of the Materials Research Society (1999).
18. F. Pschenitzka and J.C. Sturm, Spring Meeting of the Materials Research Society (1999).