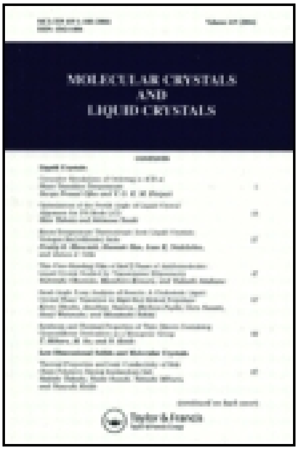


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

High Efficiency Red Phosphorescent Organic Light Emitting Diodes with Emission Structure of (TCTA/TCTA$_{0.5}$TPBi$_{0.5}$/TPBi):(pq)$_2$Ir(acac)

Ji Geun Jang [a], Jin Cheol Jeong [a], Hyun Kwan Shin [a] & Won Ki Kim [a]

[a] Department of Electronics Engineering, Dankook University, Chungnam, Korea

Version of record first published: 10 Nov 2009

To cite this article: Ji Geun Jang, Jin Cheol Jeong, Hyun Kwan Shin & Won Ki Kim (2009): High Efficiency Red Phosphorescent Organic Light Emitting Diodes with Emission Structure of (TCTA/TCTA$_{0.5}$TPBi$_{0.5}$/TPBi):(pq)$_2$Ir(acac), Molecular Crystals and Liquid Crystals, 513:1, 268-276

To link to this article: http://dx.doi.org/10.1080/15421400903212075

Mol. Cryst. Liq. Cryst., Vol. 513, pp. 268–276, 2009
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903212075

High Efficiency Red Phosphorescent Organic Light Emitting Diodes with Emission Structure of (TCTA/TCTA$_{0.5}$TPBi$_{0.5}$/TPBi):(pq)$_2$Ir(acac)

Ji Geun Jang, Jin Cheol Jeong, Hyun Kwan Shin, and Won Ki Kim
Department of Electronics Engineering, Dankook University, Chungnam, Korea

Based on the emission structure of (TCTA/TCTA$_{0.5}$TPBi$_{0.5}$/TPBi) doped with 10% (pq)$_2$Ir(acac) [hereafter, (TCTA/TCTA$_{0.5}$TPBi$_{0.5}$/TPBi):(pq)$_2$Ir(acac)], new red phosphorescent organic light emitting diodes with different host structures in thickness were fabricated and evaluated. Among the devices with various thicknesses of TCTA in a range of 50 Å ~ 150 Å in the limits of 100 Å-thick TCTA$_{0.5}$TPBi$_{0.5}$ and 300 Å-thick total host, the best electroluminescent characteristics was obtained in the device with emission structure of [TCTA (80 Å)/TCTA$_{0.5}$TPBi$_{0.5}$ (100 Å)/TPBi (120 Å)]:(pq)$_2$Ir(acac). In this device, current density, luminance, and current efficiency were found to be 98 mA/cm^2, 15,800 cd/m^2, and 16 cd/A at an applied voltage of 9 V, respectively. The maximum current efficiency was 24.5 cd/A under a luminance of 50 cd/m^2. The peak wavelength in the electroluminescence spectral distribution was 606 nm. The color coordinates were (0.62, 0.37) on the CIE (Commission Internationale de I'Eclairage) chart.

Keywords: intermixed double host; (pq)$_2$Ir(acac); red phosphorescent OLED; TCTA; TPBi

INTRODUCTION

The high efficiency of OLEDs has been demonstrated by adopting phosphors such as Ir compounds in the emission region, where heavy metal effects have led to good intersystem crossing from singlets to triplets and strong phosphorescence even at room temperature [1,2].

The present research was conducted by the research fund of Dankook University in 2009.

Address correspondence to Prof. Ji Geun Jang, Department of Electronics Engineering, Dankook University, San 29, Anseo-dong, Cheonan, Chungnam 330-714, Korea (ROK). E-mail: semicgk@dankook.ac.kr

As phosphorescent organic light emitting diodes (PhOLEDs) have the advantages of low power consumption and high luminous efficiency in comparison with fluorescent OLEDs, they are expected to be useful in the application of high illuminating light sources as well as active matrix displays [3–5]. However, the immature development for the red and blue emitting devices makes it difficult to fully use phosphorescence based technologies in the industrial application.

PhOLEDs have a four-fold luminescence compared to fluorescent OLEDs emitting only from singlet excitons [6,7]. However, in the practical devices, the luminous efficiency would be greatly reduced due to carrier injection loss, non-radiative exciton formation, exciton diffusion, triplet-triplet annihilation and so on [8–10]. Especially, red emitting PhOLEDs have some inherent problems such as low luminous efficiency and high concentration quenching effect by the molecular interaction [11,12]. Therefore, the optimum design of emission layer (materials, structures, thickness, etc.) is very important in red emitting PhOLEDs so that triplet excitons should be efficiently generated and confined in the emission layer. For example, some methods were reported to confine holes and electrons in the emission layer by inserting exciton blocking materials [13,14].

In a conventional device with single host structure, exciton formation around the outer part of emission region may arise from the injection barrier and carrier mobility differences in the emission region. Recently, various emission layers such as simple mixed or two stacked structures using double hosts (one is a hole transporting material and the other an electron transporting material) have been adopted in the PhOLEDs to avoid these problems [15–17]. But, these devices with simple mixed or two stacked double hosts still have some kinds of problems. In the device with simple mixed double hosts, triplet excitons cannot be completely confined in the emission region because exciton formation zone is extended over the entire emission region. Therefore, in terms of the confinement of excitons in the emission region, the device with simple mixed double hosts requires the establishment of exciton blocking layers on both sides of emission layer, but the insertion of exciton blocking layers gives rise to several disadvantages such as increase of driving voltage, complicated process, and so on. On the other hand, the device with two stacked double hosts have good confinement of excitons because the recombination of holes and electrons largely occurs around the interface of two hosts located in the central emission region, but it has still a problem that the exciton formation zone cannot be wide enough to obtain high luminescence due to narrow accumulated distribution of holes and electrons at the double host heterojunction.

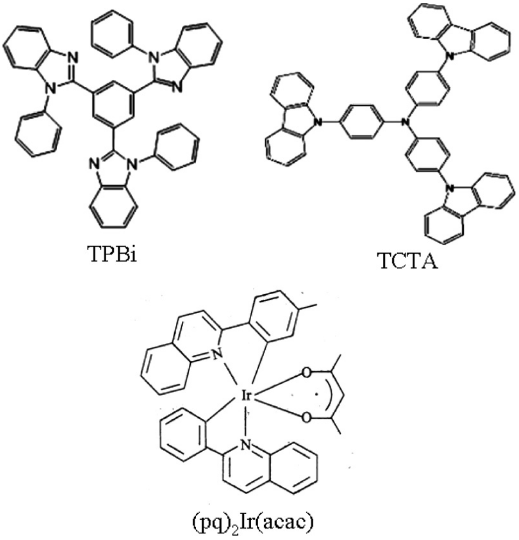
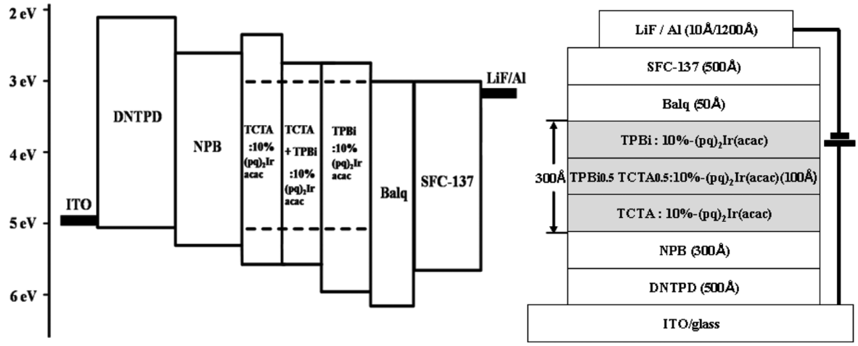


FIGURE 1 Molecular schemes used as the hosts (TCTA, TPBi) and dopant, $(pq)_2Ir(acac)$.

In this study, a new host structure of $(TCTA/TCTA_{0.5}TPBi_{0.5}/TPBi)$, that is, an intermixed double host structure with a mixed layer of $TCTA_{0.5}TPBi_{0.5}$ between double hosts of 4,4′,4″-tris(N-carbazolyl)-triphenylamine [TCTA] and 1,3,5-tris(N-phenylbenzimiazole-2-yl) benzene [TPBi] using iridium(III)bis(2-phenylquinoline-N,C2′) acetylacetonate [$(pq)_2Ir(acac)$] as a dopant was introduced to develop high efficiency red PhOLEDs. To investigate the optimum structure of host thicknesses, the devices with different thicknesses of TCTA in a range of 50 Å ~ 150 Å on the condition of 100 Å-thick $TCTA_{0.5}TPBi_{0.5}$ and total thickness of 300 Å were fabricated in the experiments. Figure 1 shows the molecular schemes of TCTA, TPBi, and $(pq)_2Ir(acac)$ which were used as the hosts and dopant.

EXPERIMENTAL PROCEDURE

The substrate with an ITO(indium tin oxide) anode of 10 Ω/sq on glass was cleaned by an ultrasonic cleaning process with acetone, methanol and isopropyl alcohol (IPA). The remaining solvent was removed by soft baking for 10 minutes at 100°C. To improve the surface morphology of the ITO transparent electrode film was plasma-treated at 200 W for two minutes with a DC bias of 37.5 V under 8 mTorr pressure of $O_2/Ar(50\%)$. The plasma treatment before deposition of the first



(a) (b)

FIGURE 2 Energy band diagram and device structure; (a) energy band diagram and (b) cross sectional view of the fabricated devices.

organic layer is expected to reduce the energy barrier for hole injection from anode and remove surface contaminations, and also improves the adhesion between ITO and organic layer. The organic thin layers and metallic layer were deposited under 5×10^{-8} Torr using *in-situ* method. After the substrate was moved from the plasma chamber into the high vacuum organic chamber, N-N′-diphenyl-N,N′-bis-[4-(phenyl-m-tolyl-amino)-phenyl]-biphenyl-4,4′-diamine [DNTPD] with thickness of 500 Å and N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl-4,4′-diamine [NPB] with thickness of 300 Å were successively deposited as a hole injection layer and a hole transport layer on the ITO electrode, respectively. In the formation of emission region, ($TCTA/TCTA_{0.5}TPBi_{0.5}/TPBi$) hosts with various thicknesses of TCTA in a range of 50 Å ~ 150 Å on the condition of 100 Å-thick $TCTA_{0.5}TPBi_{0.5}$ and total thickness of 300 Å were sequentially prepared. The doping concentration of $(pq)_2Ir(acac)$ was kept with 10% through all host layers. And then, bis(2-methyl-8-quinolinolato)(p-phenylphenolato) aluminium(III) [Balq] and SFC137 [proprietary material coded by SFC Co.) were used as a hole blocking layer and an electron transport layer, respectively. Finally, 10 Å-thick LiF and 1200 Å-thick Al were successively deposited as a cathode. The energy band diagram and structure of the fabricated devices are shown in Figure 2.

RESULTS AND DISCUSSION

The electrical properties of the devices were investigated using a Polaronix M6100 I-L-V test system (McScience). The optical properties such as luminance, emission spectrum and CIE color coordinates were evaluated using a CS-1000 spectro-radiometer (Konica Minolta) in a dark room.

The current density-voltage and luminance-voltage characteristics for the devices with different thicknesses of host layers were shown in Figures 3 and 4, respectively. In Figure 3, the experimental devices with total host thickness of 300 Å and 10% uniform doping of $(pq)_2$ Ir(acac) did not show significant difference in the current density according to the thickness variation of TCTA in a range of 50–150 Å, even though the current density slightly increased as the thickness of TCTA decreased. The device with 80 Å thick TCTA showed the current density of 98 mA/cm^2 at 9 V. However, the luminance at 9 V in Figure 4 increased from 10,000 cd/m^2 to 15,800 cd/m^2 as the thicknesses of TCTA decreased from 150 Å to 80 Å, showing the highest luminance when the thickness of TCTA was 80 Å.

Current efficiency is a convenient parameter to evaluate the electroluminescence characteristics of light emitting devices because it does not greatly depend on driving voltages. The current efficiency (η) can be calculated by the equation of $\eta = L/J$ if the current density-voltage and luminance-voltage relationships are known, where L (cd/m^2) and J (A/m^2) are luminance intensity and current density, respectively. Figure 5 represents the graph of current efficiency vs. luminance of the fabricated devices. Current efficiency tended to slightly decrease according to the increase of luminance. The highest current efficiency

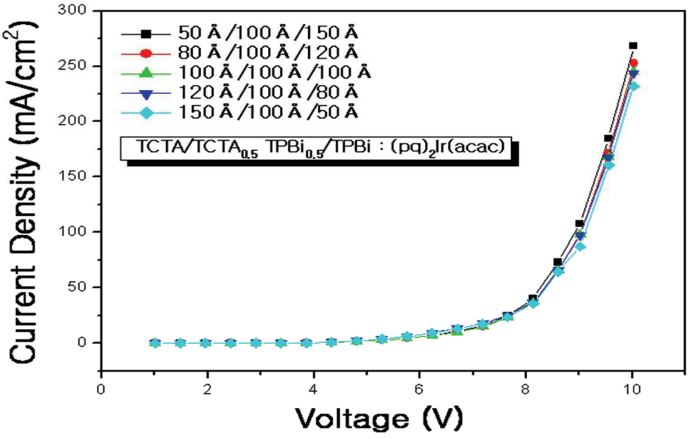


FIGURE 3 Current density versus voltage characteristic curves.

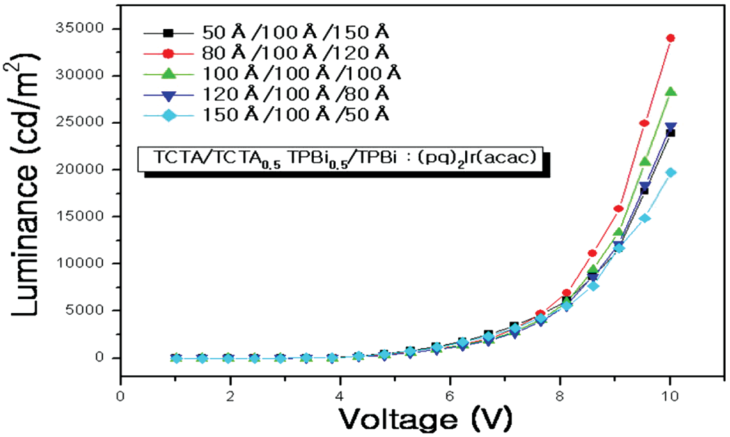


FIGURE 4 Luminance versus voltage characteristic curves.

at the given luminance was shown in the device with host structure of TCTA (80 Å)/$TCTA_{0.5}TPBi_{0.5}$ (100 Å)/TPBi (120 Å) in which the maximum current efficiency was 24.5 cd/A under a luminance of 50 cd/m^2. The device with host structure of TCTA (80 Å)/$TCTA_{0.5}TPBi_{0.5}$ (100 Å)/TPBi (120 Å) showed the current efficiency of 16 cd/A at an applied

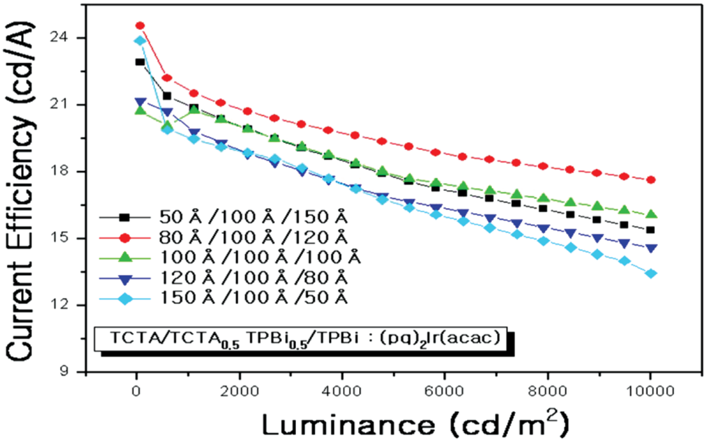


FIGURE 5 Current efficiency versus luminance characteristic curves.

voltage of 9 V and the efficiency improvement of about 1.4 times compared to the device with host structure of TCTA (150 Å)/ $TCTA_{0.5}TPBi_{0.5}$ (100 Å)/TPBi (50 Å) under the luminance of 10,000 cd/m^2. It is believed that the current efficiency of 24.5 cd/A obtained in our experiments should be one of the highest values ever achieved from the red light PhOLEDs.

The electroluminescence spectra and CIE color coordinates around 9 V for the fabricated devices were shown in Figures 6 and 7, respectively. The central wavelength and full width at half maximum of emission peak were 606 nm and 60 nm in Figure 6, which corresponds to the typical $(pq)_2Ir(acac)$ triplet emission. The color coordinates on the CIE chart were (0.62, 0.37) in Figure 7, which means the color purity of more than 95%. The electroluminescence spectra and CIE color coordinates of the fabricated devices were almost identical regardless of emission layer structures.

The excellent electroluminescent characteristics and color purity in this study could be obtained by the adoption of intermixed double host structure of ($TCTA/TCTA_{0.5}TPBi_{0.5}/TPBi$) in the emission region

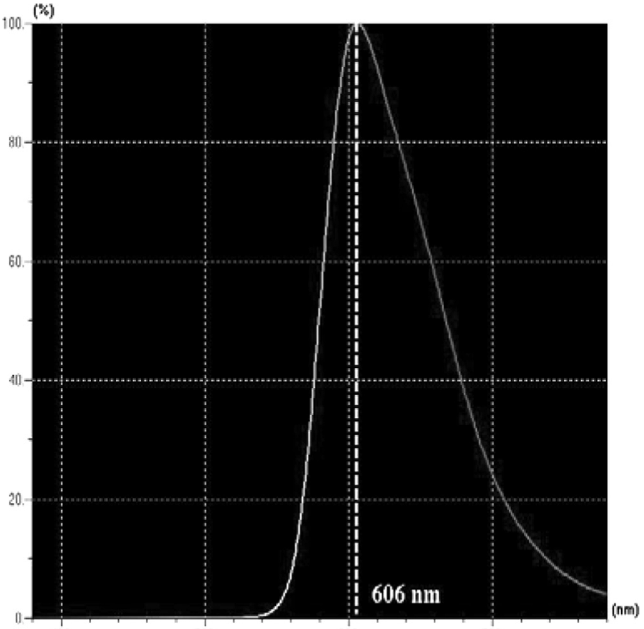


FIGURE 6 Electroluminescence spectra around 9 V for the fabricated devices.

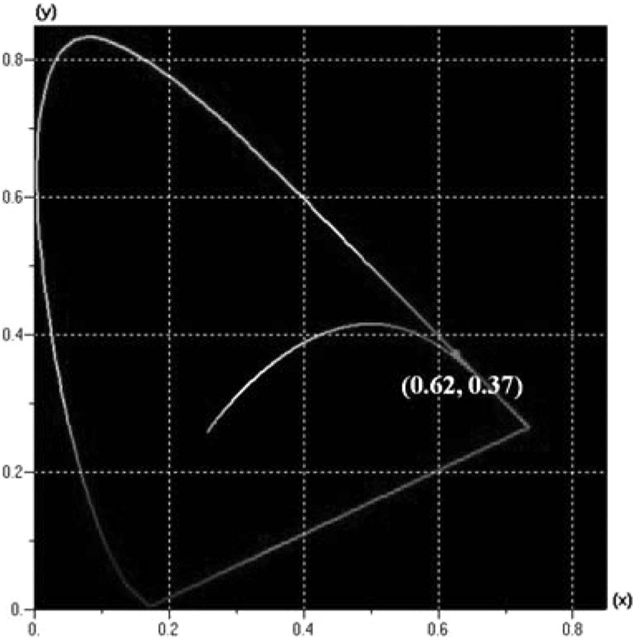


FIGURE 7 Color coordinates on the CIE chart around 9 V for the fabricated devices.

which gives effective triplet confinement and sufficient exciton formation space and the appropriate layout of each host in thickness.

CONCLUSIONS

High efficiency red emitting PhOLEDs with structure of ITO/DNTPD/NPB/EML (emission layer)/Balq/SFC137/LiF/Al were newly proposed based on the intermixed double host of TCTA/$TCTA_{0.5}TPBi_{0.5}$/TPBi doped with 10% $(pq)_2Ir(acac)$ in the emission layer.

In the experiments, the best luminance characteristics was obtained in the device with host structure of TCTA (80 Å)/$TCTA_{0.5}TPBi_{0.5}$ (100 Å)/TPBi (120 Å), which had the luminance of 15,800 cd/m^2 at 9 V and the maximum current efficiency of 24.5 cd/A under a luminance of 50 cd/m^2. The current efficiency of 24.5 cd/A can be evaluated to be the highest value ever reported in the red emitting PHOLEDs. High luminance and current efficiency of the fabricated devices could be obtained due to the adoption of new emission structure which can give the effective confinement of triplet excitons and sufficient space of exciton formation.

REFERENCES

[1] Wilson, J. S., Dhoot, A. S., Seeley, A. J. A. B., Khan, M. S., Köhler, A., & Friend, R. H. (2001). *Nature*, *413*, 828.

[2] Lu, W., Mi, B.-X., Chan, M. C. W., Hui, Z., Che, C.-M., Zhu, N., & Lee, S.-T. (2004). *J. Am. Chem. Soc.*, *126*, 4958.

[3] Baldo, M. A., O'Brien, D. F., You, Y., Shoustikov, A., Sibley, S., Thompson, M. E., & Forrest, S. R. (1998). *Nature*, *395*, 151.

[4] O'Brien, D. F., Baldo, M. A., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *74*, 442.

[5] Baldo, M. A., Lamansky, S., Burrows, P. E., Thompson, M. E., & Forrest, S. R. (1999). *Appl. Phys. Lett.*, *75*, 4.

[6] Gong, X., Ostrowski, T. C., Bazan, G. C., Moses, D., Heeger, A. J., & Liu, M. S. (2003). *Adv. Mater.*, *15*, 45.

[7] Tsuboyama, A., Iwawaki, H., Furugori, M., Mukaide, T., Kamatani, J., Igawa, S., Moriyama, T., Miura, S., Takiguchi, T., Okada, S., Hoshino, M., & Ueno, K. (2003). *J. Am. Chem. Soc.*, *125*, 12971.

[8] Sajoto, T., Djurovich, P. I., Tamayo, A., Yousufuddin, M., Bau, R., Thompson, M. E., Holmes, R. J., & Forrest, S. R. (2005). *Inorganic Chemistry*, *44*, 7992.

[9] Namdas, E. B., Ruseckas, A., Samuel, I. D. W., Lo, S.-C., & Burn, P. L. (2005). *Appl. Phys. Lett.*, *86*, 091104.

[10] Kalinowski, J., Stampor, W., Cocchi, M., Virgili, D., Fattori, V., & Di Marco, P. (2002). *Phys. Rev.*, *B 66*, 235321.

[11] Su, Y., Huang, H., Li, C., Chien, C., Tao, Y., Chou, P., Datta, S., & Liu, R. (2003). *Adv. Mater.*, *15*, 884.

[12] Song, Y., Yeh, S., Chen, C., Chi, Y., Liu, C., Yu, J., Hu, Y., Chou, P., Peng, S., & Lee, G. (2004). *Adv. Funct. Mater.*, *14*, 1221.

[13] Mitsuya, M., Suzuki, T., Koyama, T., Shirai, H., Satuki, M., Taniguchi, Y., Satsuki, M., & Suga, S. (2000). *Appl. Phys. Lett.*, *77*, 3272.

[14] Adamovich, V. I., Cordero, S. R., Djurovich, P. I., Tamayo, A., Thompson, M. E., D'Andrade, B. W., & Forrest, S. R. (2003). *Organic Electron.*, *4*, 45.

[15] Matsushima, H., Naka, S., Okada, H., & Onnagawa, H. (2005). *Current Applied Physics*, *5*(4), 305.

[16] Zhou, X., Qin, D. S., Pfeiffer, M., Blochwitz, J., Werner, A., Crechsel, J., Maennig, B., Leo, K., Bold, M., Erk, P., & Hartmann, H. (2002). *Appl. Phys. Lett.*, *81*, 4070.

[17] Kawamura, Y., Yanagida, S., & Forrest, S. R. (2002). *J. Appl. Phys.*, *92*, 87.