International Journal of Thin Film Science and Technology

Volume 2
Issue 2 *May 2013*

Article 2

2013

Photolithography versus lift off process for patterning of sputtered indium tin oxide for flexible displays

Mariya Aleksandrova
Technical University of Sofia, Bulgaria, Department of Microelectronics, 8, Kliment Ohridski blvd, bl. 1,, m_aleksandrova@tu-sofia.bg

Georgy Kolev
Technical University of Sofia, Bulgaria, Department of Microelectronics, 8, Kliment Ohridski blvd, bl. 1, m_aleksandrova@tu-sofia.bg

Ivelina Cholakova
Technical University of Sofia, Bulgaria, Department of Microelectronics, 8, Kliment Ohridski blvd, bl. 1,, m_aleksandrova@tu-sofia.bg

Georgy Dobrikov
Technical University of Sofia, Bulgaria, Department of Microelectronics, 8, Kliment Ohridski blvd, bl. 1, m_aleksandrova@tu-sofia.bg

Georgy Bodurov
Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Science, Sofia, Bulgaria, bul. "Tsarigradsko Chaussee", 72., m_aleksandrova@tu-sofia.bg

International Journal of Thin Films Science and Technology

http://dx.doi.org/10/12785/ijtfst/020202

Photolithography versus lift off process for patterning of sputtered indium tin oxide for flexible displays

Mariya Aleksandrova [1], Georgy Kolev[1], Ivelina Cholakova[1], Georgy Dobrikov [1] and Georgy Bodurov[2]

[1]Technical University of Sofia, Bulgaria, Department of Microelectronics, 8, Kliment Ohridski blvd, bl. 1, phone +35929653085
[2]Central Laboratory of Solar Energy and New Energy Sources, Bulgarian Academy of Science, Sofia, Bulgaria, bul. "Tsarigradsko Chaussee", 72.

E-mail: m_aleksandrova@tu-sofia.bg

Received: 12 Dec. 2012, Revised: 19 Dec 2012; Accepted: 13 Apr. 2012
Published online: 1 May 2013

Abstract: Indium tin oxide (ITO) is deposited by RF sputtering on polyethylene terephthalate substrate as transparent electrode for flexible display applications. The produced coatings are patterned in form of digits for seven-segmented indication via conventional photolithography and lift off process. The influence of the exposure dose, etching and stripping solution on the electrophysical properties of ITO films and achieved image resolution were investigated. The sheet resistance increases from 66.5 Ω/square to 101.9 Ω/square after wet etching. The undercut is 6μm for 2 mm wide segment, which is satisfactory for digital indication. After lift off, no undercut is observed, but ITO sheet resistance increases to 197 Ω/square. In both cases ITO film's transmittance for the visible light remains higher than 89 %.

Keywords: sputtered ITO, flexible display, ITO patterning.

1. Introduction

When displays are in question, it is very popular to consider flat panel ones and more concrete the promising organic based displays. In contrast to the epitaxial growth of single crystal inorganic electroluminescent semiconductors, organic electroluminescent films are easy for deposition via cheap techniques like spin-coating, spray deposition and ink-jet printing [1,2],. Nowadays, a tendency to make the displays thinner and lighter, and to replace conventional paper with "electronic paper", by using of flexible substrates is imposed. However, many problems still have to be solved with the replacing of the glass substrates by polymeric ones. One of them is the preparation of high quality conductive transparent electrode from indium-tin oxide (ITO) on the flexible substrate. Many deposition methods have been developed for optimal combining of conductivity and transparency [3,4], but most of them require relatively high temperatures. One of the most spread methods is vacuum sputtering with its varieties – magnetron, direct current and radiofrequency (RF). The specificity in case of flexible substrate is connected with preserving of the low melting point flexible materials caused by the plasma temperature. Many approaches have been proposed for keeping the deposition temperatures as low as possible [5, 6]. Another problem which has to be solved is the proper coating patterning, according to the display's application without damage the substrate. Many efforts are made for patterning of ITO deposited on glass

for the needs of TV and laptop screens, video walls, information boards, seven segments digital indications and so on [7].

In the case of flexible substrate the patterning can not be performed by using shadow mask in contact with the substrate surface during deposition, because of possibility for overheat and melt. If the mask is positioned at certain distance from the surface, scattering of the sputtered particles and irregular image shapes could arise. For smaller features like dots (pixels) this approach is absolutely inapplicable. High plasma etching is also inapplicable for prevention of heating. Also the method is expensive and requires specific preliminary preparation of patterned mask layer, which cannot be photoresistive [8]. The conventional photolithography and lift off still remain one of the processes to configure the electrode films in the desired manner. However, the processes still have to be optimized without interfering the electrophysical parameters of as deposited ITO. In the literature this is seldom investigated for layers deposited on flexible and easy damageable substrates.

In this paper we present results from patterning of RF sputtered indium-tin oxide on flexible polyethileneterephtalate (PET) substrates by forward (conventional) and reverse (lift off) photolithography. We investigated the changes in the ITO film's resistivity and the size of the transferred geometrical features after applying both structurizing technologies. We made comparison of specific and sheet resistance after UV exposure, wet etching and photoresist stripping steps.

2. Materials and methods

Highly flexible sheets from polyethyleneterephtalate foil, having melting point of 80^{o}C, were cut to sizes 2.5 cm x 2.5 cm and cleaned. Detergent solution of hydrogen peroxide:ammonia: distilled water in 1:1:3 ratio was prepared in addition to treatment in ultrasonic cleaner for 90 seconds for increased adhesion of the layers to the substrate's surface. ITO films were prepared by RF reactive sputter system Leybold Hereaus A400VL. The target consists of In_2O_3 and SnO_2 in weight proportion of 95:5 mol%. The sputtering power was decreased to 210 W in comparison to our previous developed technology for deposition of ITO electrode on glass. Here, the RF power was set to 60 W (target voltage 500 V and plasma current 120 mA) at deposition time of 20 minutes. The base pressure was 8.10^{-6} Torr, the oxygen pressure is 2.10^{-4} Torr and the total pressure of reactive gas and sputtering inert (argon) gas was $2.5.10^{-2}$ Torr. In this way the substrate temperature during film growth was lower then the temperature of PET's mechanical deformation. For the photolithography and lift off processes positive photoresist AZ 1500 was spin-coated at 2000 rpm per 30 sec. Oxalic acid (HC_2O_4) 5.4 g was dissolved in 100 ml distilled water for etching solution (0.6M). Exposure source with power 250 W at UV wavelength of 365 nm was used.

The thickness of ITO film was measured 150 ± 1 nm. The refractive index, extinction coefficient and physical thickness of the films were determined simultaneously from transmittance and reflectance spectra of the sample deposited on transparent substrates (optical glass) and the reflectance spectra of the corresponding films deposited on opaque silicon substrates [9,10]. The spectra were recorded by a high precision Cary 5E spectrophotometer at normal light incidence in the wavelength region λ = 400 – 800 nm, with an accuracy of 0.1 and 0.5 %, respectively. The specific and sheet resistances of the films were measured by using four-point probe FPP 500. For bonds identification FTIR spectroscopy analysis were performed by Shimadzu FTIR spectrophotometer IRPrestige-21 in reflection mode. Layers morphology

was observed under scanning electron microscopy JEOL - JXA733 at accelerating voltage 25 kV, combined with energy-dispersive X-ray spectroscopy (EDS) system for elemental analysis. The composition of the films was investigated by X-ray diffractometer PX160. Ni-filtered Cu kα radiation was used at 35 kV and 15mA with λ = 0.154184 nm.

Figure 1 shows the consequence of technological operations for segmenting of ITO by conventional and reverse photolithography. As can be seen, in the first case, already deposited ITO film undergo patterning through photomask, but at the second case only the photoresistive film is patterned through photomask, followed by ITO sputtering and stripping of bilayer parts photoresist/ITO.

During the photoresist deposition on the PET surface wetting problems occurred which imposed work at lower revolutions per minute of the spin-coater (2000 rpm). Lower viscosity photoresists are preferable to avoid deposition of thick films, which require longer exposure and etching times. In this case 0.8 μm photosensitive film was produced for its viscosity of 6.3 cSt at 25°C. Drying conditions had to be modified, according to the lower melting point of the PET, so 70oC for 15 minutes in convection air oven was conducted to remove the residual solvent. Flexible photomask with digit image is aligned for contact photithography. The exposure source illuminates 45 sec. Developer solution of 1% KOH was used to remove exposed with UV light areas by dipping for 20 seconds. Hard baking process was also modified and conducted at decreased temperature of 70^{o}C for 15 min, same like the soft baking. In this way it is expected lower acids resistivity, so the time for treatment in the etching solution must be as short as possible. Conventional for ITO etching solutions cannot be used when the film is deposited on polymer substrate, because they usually consist of strong acids, like mixture of HNO_3 and HC1 [11] and can dissolve the substrate. Therefore, not so aggressive acids are recommended, like oxalic acid for example [12].

3. Results and Discussion

The average etching rate for the prepared etching solution is 17 nm/min. this value is in good agreement with already reported results for magnetron sputtered ITO on glass, etched at same etching solution concentration at room temperature (22^{o}C) [9]. This behaviour is connected with the film microstructure. It is well known that highly crystalline structures are not easy etchable. Therefore, in our case, this manner of relatively fast film's removing is due to the amorphous structure of the as deposited ITO on PET substrate, formed due to the lower than the usual sputtering temperatures in the vacuum chamber. The amorphous structure is identified by XRD analysis (figure 2). The etch rate can be increased by warming the etching solution, but high undercut is expected, which is the reason to not use this approach.

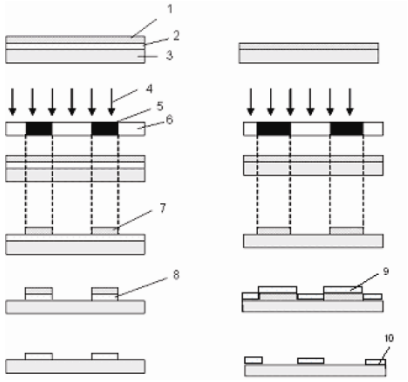


Figure 1: Steps of the pattering processes – forward photolithography (left) and reverse (lift off) photolithography (right). 1 – Photoresistive film; 2 – sputtered ITO; 3 – PET substrate; 4 – UV light exposure; 5 – non-transparent areas of the photomask; 6 – photomask alignment; 7 – photoresistive coating, which is not soluble after development; 8 – patterned ITO after isotropic wet etching; 9 – ITO deposited over patterned photoresist; 10 – patterned ITO with inverse configuration after lift off.

Sheet and specific resistance are connected with the microstructure and chemical composition of the film. As will be shown, in this case film's structure and composition are influenced not only by the deposition conditions, but also by the patterning conditions. Our previous investigations [13] showed that exposure with UV light can introduces energy enough to initiate reorganization in the ITO particles at its surface and the exposed layers reveal crystallization. Microcrystalline like formations with dimensions ~1μm are observed in the places where UV rays expose the ITO surface under the illuminated photoresist. This effect occurs after the exposure step, when the duration of exposure has been up to 1 minute and the density of the illuminated photoresist decreases. UV light partially penetrates into ITO film through the photoresist which already has been undergone photochemical reaction. The above described effect can be observed on the SEM micrograph (figure 3), showing part from ITO segment, which is not etched. This local structural change results in arising peaks in the XRD diffractogram, which confirms the SEM results. Typical bands can be seen at 2Theta = 24^o and 28^o, where are the strongest peaks. They are related with orientation of the formed crystals preferentially in (222) direction [14]. These peaks are actually caused by scattering of the X-rays from the grain boundaries. Decreasing of the sheet and specific resistance in comparison with the values of as deposited ITO before patterning is ascribed to the initial crystallization. It seems that the sheet resistance is in reverse dependence with the degree of crystal formation (i.e. UV exposure time). However there is a limit in the exposure time at constant power, after which the ITO film's conductivity begins to worsen vastly. The peaks around 45^o and 55^o are due to the plastic PET substrate. At no UV treatment there is no texture of the film, which can be seen from the lack of diffraction spectra in the XRD investigation.

Table 1 summarizes the values of the sheet and specific resistance of ITO film before pattering and after photolithographic and lift off processing. The values of both parameters are averaged from measurements at least in three points from the remained coating (upper, middle and lower part of the segments – see figure 5).

Exposure more than 2 minutes is close to the critical limit for the substrate's damage, because breaks carbon bonds in it, they penetrate by diffusion to the ITO film and increase its resistance almost twice. This observation is confirmed by elemental EDS analysis, which indicate small concentration of carbon atoms in the ITO layer, diffusing from the substrate (figure 4). Detected concentration is small, because UV illumination is local and cause changes only on restricted by the photomask areas, passing UV rays. The carbon atoms act like impurities in ITO lattice and change the film's resistance.

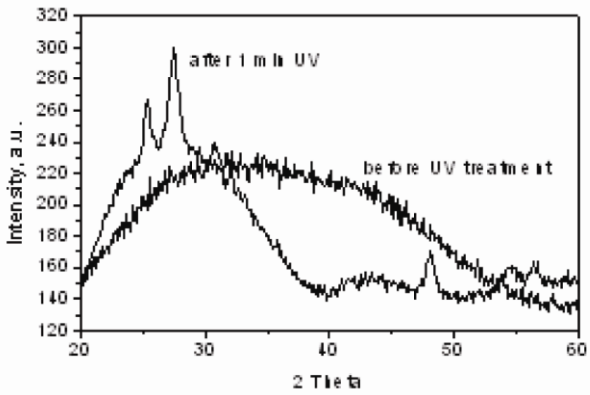


Figure 2: XRD spectra of unexposed (as deposited) and up to 1 min locally exposed ITO film on PET.

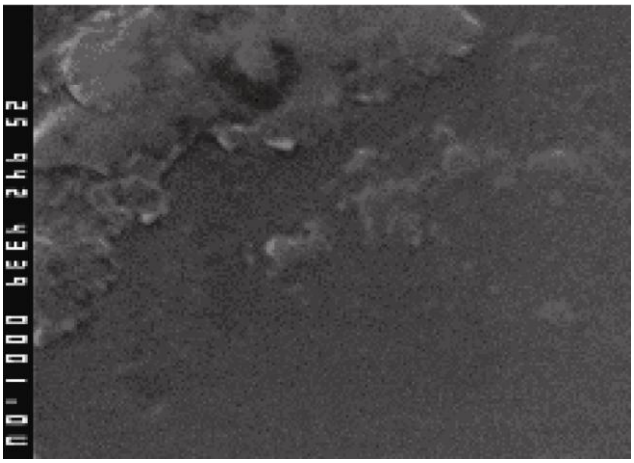


Figure 3: SEM image of exposed during photolithography ITO film, deposited on PET.

Finally, after etching process undercut effect is observed from the microscopic photography of the patterned ITO, restricting the application of the photolithography for patterns, which have millimetre dimensions like used digital segments (figure 5). Again, a slight increase of the resistance was observed, probably because of the isotropic nature of the used oxalic acid as etching liquid.

Table 1: Changes in the resistance before and after different steps of the patterning processes.

Quantity	Before pattering	After UV exposure up to 1 min	After UV exposure over 2 min	After wet etching	After lift off	After heating up to 70°C after lift off
Sheet resistance, Ω/square	66.5	50	94.2	101.90	197.00	114
Specific resistance, Ω.cm	0.163	0.101	0.196	0.220	0.667	0.280

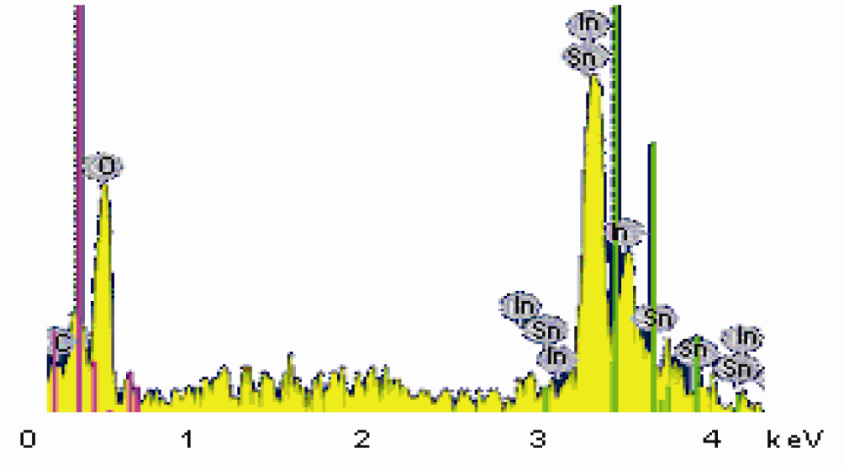


Figure 4: Elemental EDS analysis of overexposed system PET/ITO/photoresist after photolithography.

Because the behaviour of the oxalic acid is isotropic, so undercut effect is expected during etching. For the preferable ITO thickness of 150 nm for display applications [15] the undercut for 8 minutes treatment (time for fully etching of unprotected ITO) is 6 μ m for every of both edges of 2 mm wide strip shaped pattern (figure 5). For larger images like digital indicators or informational video screens this undercut is not crucial. However, for the contemporary graphical displays with resolution, corresponding to pixel dimensions between 9 and 24 μ m, this undercut is unacceptable. This is the reason for avoiding of the standard photolithography for such types of displays.

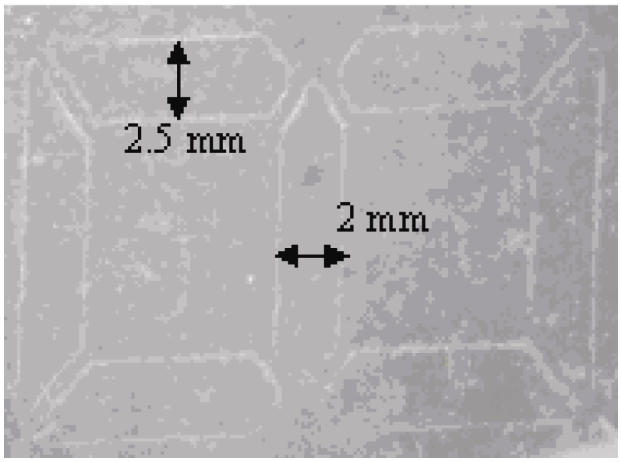
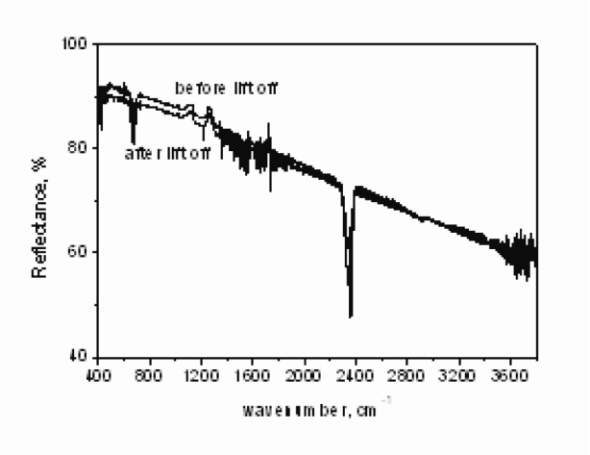


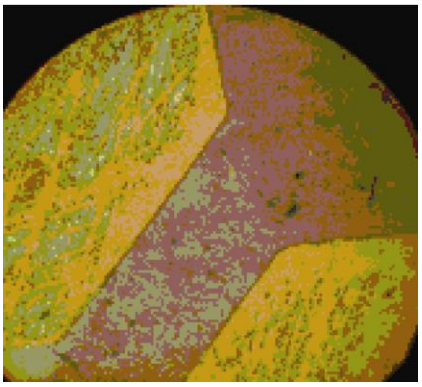
Figure 5: Optical microscope image of ITO segments patterned with photolithography. The edges are jagged

Because the behaviour of the oxalic acid is isotropic, so undercut effect is expected during etching. For the preferable ITO thickness of 150 nm for display applications [15] the undercut for 8 minutes treatment (time for fully etching of unprotected ITO) is 6 μ m for every of both edges of 2 mm wide strip shaped pattern (figure 5). For larger images like digital indicators or informational video screens this undercut is not crucial. However, for the contemporary graphical displays with resolution, corresponding to pixel dimensions between 9 and 24 μ m, this undercut is unacceptable. This is the reason for avoiding of the standard photolithography for such types of displays.

As mentioned before, an alternative way of ITO patterning is lift off processing, where practically there is no wet chemical etching and therefore undercut effects are absent. However, there are other specificities here: 1) inverse photomask must be used; 2) ITO film with the desired thickness of 150 nm is hardly stripped at the boundaries with the carrier photoresist. This implies at least twice longer rinsing times in acetone (50 sec) for complete removing of the photoresist/ITO binary layer and achieving of abrupt shapes at the edges. Acetone molecules penetrate within the pores or irregularities on the ITO film's surface, interact with ITO particles and change film resistance from 66.5 to 197 Ω/square. Evidence for this is the FTIR spectrum of ITO after lift off process (figure 6a), which shows typical bands at 1214, 1363, 1624 and 1732 cm-1, corresponding to acetone presence and different acetone-oxygen bonds. Additional increase of the sheet resistance is received from residual photoresist get onto ITO surface and stuck on it during rinsing (figure 6b). It is necessary to heat the treated substrate at 70 oC for 10 min for evaporation of the residual acetone and other impurities. In this way sheet resistance falls to 114 Ω/square. The latter is still high enough and can causes low injection efficiency at the expense of high display resolution, restricted only by the used exposure system, but not by the process itself.



(a)



(b)

Figure 6: a) FTIR spectra of ITO before and after lift off process; b) photoresist contaminations on ITO surface during rinsing of lift off treated substrate; c) abrupt edges of ITO segments after stripping of the photoresist.

Although the applied photolithographic processes interferes light transmittance in the visible wavelength region, the transparency still exceeds 89% and therefore the ITO coating can be used as front panel observing electrode.

4. Conclusion

In summary, the conventional photolithography doesn't change the resistance out of the allowable limits, but after lift off process it increases above the permissible value for display electrode and reaches 197 Ω/square. This can be ascribed to the longer time of dipping in acetone for removing of the photoresist deposited under the ITO film. However, the edges of the patterns are very sharp in comparison to the obtained after oxalic acid wet chemical etching, where undercut of 6 μm occurs because of the isotropic etcher. The lift off is faster technological process in comparison to the conventional photolithography for ITO pattering, because skip steps like hard backing and etching, and directly photoresist stripping is conducted.

Acknowledgment

The work is financial supported by grant ДМУ 03/5 – 2011 of Fund "Scientific Research", Bulgarian Ministry of Education, Youth and Science. The authors are thankful to the colleagues from Institute of Metal Science, Institute of Physical Chemistry and Institute of Electrochemistry for the performed SEM, EDS and XRD analysis.

References

[1] M. Tsai, C. Liu, M. Hsu, T. Chow, Appl. Phys. Lett. **82** (2003) 550-552.

[2] M. Shakutsui, K. Fujita, T. Tsutsui, Jpn. J. Appl. Phys. **45** (2006) 790-792.

[3] D. Raoufi, A. Kiasatpour, H. Fallah, A. Rozatian, Appl. Surf. Sci. **253** (2007) 9085-9090.

[4] M. Keum, J. Han, J. Korean Phys. Soc. **53** (2008) 1580-1583.

[5] K. Fang, H. Lin, F. Gan, H. Chiu, *Proc. of ASID '06, 8-12 Oct, New Delhi* (2006) 302.

[6] S. Wakeham, M. Thwaites, B. Holton, C. Tsakonas, W. Cranton, D. Koutsogeorgis, R. Ranson, *Thin Solid Films* **518** (2009) 1355-1358.

[7] J. Chae, S. Appasamy, K. Jaina, Appl. Phys. Lett. **90** (2007) 261102.

[8] V. Videkov, M. Aleksandrova, S. Andreev, K. Denishev, Handbook of technology of microelectromechanical systems, Technical University Publishing House, Sofia, 2012.

[9] I. Konstantinov, Tz. Babeva, S. Kitova, Appl. Opt. **37** (1998) 4260-4267.

[10] Tz. Babeva, S. Kitova, I. Konstantinov, Appl. Opt. **40** (2001) 2682-2686.

[11] J. Lan, J. Kanicki, A. Catalano, J. Keane, W. Boer, T. Gu, J. Electron. Mater. **25** (1996) 1806-1817.

[12] E. Nishimura, H. Ohkawa, P. Song, Y. Shigesato, Thin Solid Films **445** (2003) 235-240.

[13] M. Aleksandrova, I. Cholakova, G. Bodurov, G. Kolev, G. Dobrikov accepted in Int. *J. Electron. Elec. Eng.*

[14] A.K. Kulkarnia, K. H. Schulz, T.S. Lim, M. Khan, Thin Solid Films **345** (1999) 273-277.

[15] H. Lee, O. Park, Vacuum **80** (2006) 880-887.