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PATENT APPLICATION/TECHNICAL DIGEST PUBLICATION RELEASE REQUEST

FROM: Associate Counsel (Patents) (1008.2)
TO: Associate Counsel (Patents) (1008.2)

Via: (1) James Horwitz (Code 6372)
(2) Division Superintendent (Code 6300)
(3) Head, Classification Management & Control (Code 1221)

SUBJ: Patent Application/Technical Digest entitled: **"PULSED LASER DEPOSITION OF TRANSPARENT CONDUCTING THIN FILMS ON FLEXIBLE SUBSTRATES"** Request for release for publication.

REF: (a) NRL Instruction 5510.40C
(b) Chapter 6, ONRINST 5870.1C

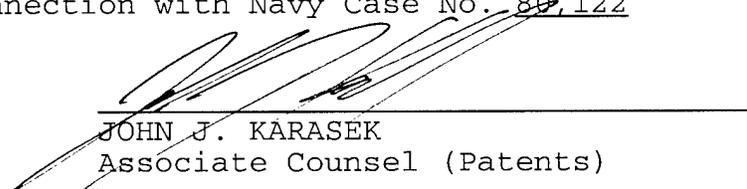
ENCL: (1) Copy of Patent Application/Technical Digest

1. In accordance with the provision of references (a) and (b), it is hereby requested that the subject Patent Application/Technical Digest be released for publication.

2. It is intended to offer this Patent Application/Technical Digest to the National Technical Information Service, for publication.

3. This request is in connection with Navy Case No. 89,122

1/25/01
(date)



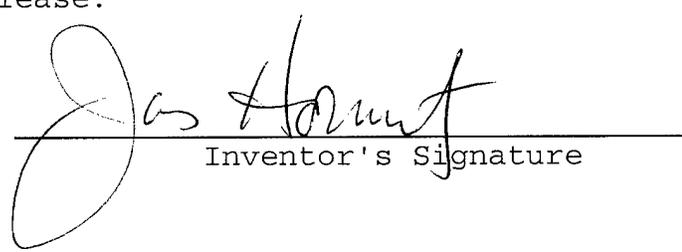
JOHN J. KARASEK
Associate Counsel (Patents)

FIRST ENDORSEMENT

Date:

FROM: James Horwitz (Code 6372)
TO: Division Superintendent (Code 6300)

1. It is the opinion of the Inventor(s) that the subject Patent Application/Technical Digest (is) (is not) classified and there is no objection to public release.



Inventor's Signature

SECOND ENDORSEMENT

Date:

FROM: Division Superintendent (Code 6300)
TO: Classification Management & Control (Code 1221)

1. Release of Patent Application/Technical Digest (is) (is not) approved.
2. To the best knowledge of this Division, the subject matter of this Patent Application/Technical Digest (has) (has not) been classified.
3. This recommendation takes into account military security, sponsor requirements and other administration considerations and there in no objection to public release.



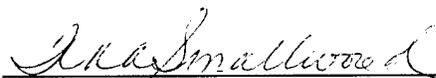
Division Superintendent

THIRD ENDORSEMENT

Date:

FROM: Head, Classification & Control (Code 1221)
TO: Associate Counsel (Patents) (1008.2)

1. This Patent Application/Technical Digest is authorized for public release.



Head, Classification, Management & Control

1
2 PULSED LASER DEPOSITION OF TRANSPARENT CONDUCTING THIN FILMS ON
3 FLEXIBLE SUBSTRATES
4

5 **Background of the Invention**

6 **1. Field of the Invention**

7 The invention relates generally to the deposition of transparent conducting thin films on
8 flexible substrates by pulsed laser deposition (PLD), and more particularly to the deposition of
9 thin films such as transparent conducting oxides (TCO) on flexible substrates.
10

11 **2. Description of the Related Art**
12

13 Tin doped indium oxide (ITO) and aluminum doped zinc oxide (AZO) thin films,
14 because they combine both transparent and conducting properties, have been widely used as
15 transparent conducting electrodes in optoelectronic devices such as solar cells and flat panel
16 displays (FPDs), surface heaters for automobile windows, camera lenses and mirrors, as well as
17 transparent heat reflecting window material for buildings, lamps, and solar collectors. They are
18 also widely utilized as the anode contact in organic light-emitting diodes (OLEDs). There are
19 several deposition techniques used to grow these TCO films, including chemical vapor
20 deposition (CVD), magnetron sputtering, evaporation, and spray pyrolysis. These techniques
21 require either a high substrate temperature during deposition or a post deposition annealing

1 treatment of the films at high temperatures. These high temperatures generally damage the
2 surfaces of both the substrate and the film. In the typical organic light emitting diode (OLED)
3 geometry, the TCO films are used as the anode contact and are deposited directly onto the
4 transparent glass substrate. In some cases, it is desirable to reverse the device geometry in which
5 case the TCO film would have to be deposited on top of the organic emitting layer. In this case
6 the sputtering technique cannot be used to grow the electrode film because the energetic species
7 (>100 eV) from the sputter target damage the organic layer. This limitation can be overcome by
8 using PLD to deposit the top electrode because the PLD has low energy species due to high
9 background gas pressure.

10 Glass substrates have been widely used for the development of OLEDs. However, glass
11 substrates are unsuitable for certain applications such as electronic maps and portable computers.
12 Where flexibility or safety issues are important glass is very brittle and cannot be used since it
13 cannot be easily deformed, or is too heavy, especially for large area displays. These
14 disadvantages can be overcome using either plastic or thin metal foil substrates, which can be
15 very lightweight. To develop an advanced OLED technology based on plastic or metal foil
16 supports requires the TCO material to be either grown directly on plastic or on top of the organic
17 emitting layer for metal foil geometry. Passive and active matrix displays such as liquid crystal
18 displays (LCDs) and organic electroluminescent displays will benefit greatly from the use of
19 flexible substrates.

20 Recently, the growth of ITO films on plastic substrates by sputtering has been reported
21 by T. Minami et al., *Thin Solid Film*, Vol. 270, page 37 (1995), and J. Ma, *Thin Solid Films*, vol.
22 307, page 200 (1997) (both incorporated herewith by reference) with a rough surface

1 morphology (approximately 6 nm of RMS surface roughness) and a high electrical resistivity of
2 $7 - 20 \times 10^{-4} \Omega\text{-cm}$. The rough surface morphology and high resistivity of the sputter-deposited
3 ITO films significantly degrade the performance of the OLED.

4 The current method of depositing TCO films on plastic substrates by sputtering produces
5 a rough surface morphology and high resistivity, which degrades the performance of the OLED.

6 Therefore, there is a strong need for transparent conducting thin films on flexible substrates
7 which exhibit a smooth surface, high optical transparency and low electrical resistivity, which
8 are suitable for use in OLEDs and methods of producing same.

9

10 **Objects of the Invention**

11 According to the present invention, the foregoing and other objects are attained by
12 providing TCO thin films on flexible substrates which exhibit a smooth surface, higher optical
13 transparency and lower electrical resistivity and methods of making same.

14 It is an object of the present invention to provide methods for depositing TCO films on
15 flexible substrates to produce a surface with a smooth surface, higher optical transparency and
16 lower electrical resistivity.

17 Additional objects and advantages of the invention will be set forth in part in the
18 description which follows, and, in part, will be obvious from the description, or may be learned
19 by practice of the invention.

20

21

1 plotted as a function of oxygen deposition pressure (P_{O_2}). All films were deposited at 25° C.

2 There is an optimum oxygen deposition pressure at which the resistivity is a minimum, which is
3 observed at 40 mTorr in this system. The film thickness is about 200 nm for all films.

4 Figure 3 shows optical transmission spectra of ITO and AZO films deposited on PET
5 substrates. Both films were deposited at 25°C and in 40 mTorr of oxygen. The average
6 transmission in the visible range (400-700 nm) is 90% and 91% for the ITO and AZO films,
7 respectively. The film thickness is about 100 nm for all films.

8 Figures 4(a), 4(b) and 4(c) show the atomic force microscopy (AFM) images (2 μm x 2
9 μm) of: Fig. 4(a) a bare PET substrate; Fig 4(b) an ITO film coated on PET; and Fig. 4(c) an
10 AZO film coated on PET by PLD. The rms surface roughness of ITO and AZO films is about 3
11 nm and 4 nm, respectively while that of the bare PET substrate is about 9 nm. Note that the
12 scale in the z-direction (50 nm/div.) is greatly expanded with respect to the scales in the x and y
13 directions (1.0 $\mu\text{m}/\text{div.}$).

14 Figures 5(a) and 5(b) show the atomic force microscopy (AFM) images (2 μm x 2 μm)
15 of: Fig. 5(a) a bare flexible Si substrate (25 nm thick) and Fig. 5(b) an ITO film coated on
16 flexible Si by PLD. The rms surface roughness is about 1.3 nm and 0.9 nm for Si substrate and
17 ITO film, respectively.

18 Figures 6(a) and 6(b) show the atomic force microscopy (AFM) images (300 nm x 300
19 nm) of: Fig. 6(a) a bare Ag foil and Fig. 6(b) an ITO film coated on Ag foil by PLD. The rms
20 surface roughness is about 0.8 nm and 0.7 nm for Ag foil and ITO film, respectively.

21 Fig. 7(a) shows an OLED device configuration.

1 Fig. 7(b) shows the chemical structures of the organic materials used in Fig. 7(a).

2 Fig. 8(a) is a graph of the current density (J) versus applied voltage (V).

3 Fig. 8(b) is a graph of luminance (L) versus applied voltage (V) characteristics for
4 devices based on PLD ITO/ PET and commercial ITO/glass.

5
6 **Description of the Preferred Embodiments**

7
8 The present invention comprises a method of depositing transparent conducting films on
9 flexible substrates using pulsed laser deposition and a transparent conducting film deposited on a
10 flexible substrate, and OLED devices incorporating a transparent conducting film deposited on a
11 flexible substrate.

12 Example 1

13 A KrF excimer laser (248 nm and 30 ns FWHM) was operated at 10 Hz and focused
14 through a 50-cm focal lens onto a rotating target at 45° angle of incidence. The energy density of
15 the laser beam at the target surface was maintained at 1 J/cm². The target-to-substrate distance
16 was 5.8 cm. The target composition for deposition of the ITO film was 5 wt% SnO₂-doped In₂O₃
17 and the oxygen deposition pressure was 40 mTorr.

18 Using the above target composition and oxygen pressure, ITO was deposited on flexible
19 substrates such as polyethylene terephthalate (PET) by PLD at room temperature. The
20 temperatures used for deposition ranged from approximately 25 – 125° C. AFM measurement
21 indicated that the RMS surface roughness of the PLD ITO films on PET is about 2 – 3 nm, which
22 is a half of that measure with commercially available sputter-deposited ITO films on PET.

1 Furthermore, the electrical resistivity of the PLD ITO films on PET is observed to be 6.0×10^{-4}
2 Ω -cm, which is the lowest ever reported for films deposited on flexible substrates at room
3 temperature by any method. In addition, the optical transmission of the PLD ITO films on PET is
4 greater than 85% in the visible range (400-700 nm). AZO films grown by PLD on PET substrates
5 at room temperature show very smooth surface morphology (RMS surface roughness of 2-3 nm),
6 with low resistivity ($7 \times 10^{-4} \Omega$ -cm) and high transparency (>87%).

7 ITO and AZO films grown by PLD deposited on PET demonstrated a planarizing effect.
8 On PET, the surface roughness is reduced from 8-10 nm for the uncoated material to 3 nm for the
9 coated material. These smooth ITO films can significantly improve the device performance of
10 flat panel displays such as LCDs and OLEDs.

11 ITO and AZO films deposited on PET substrates show approximately a factor of 3
12 improvement (2 nm vs. approximately 6 nm) in surface morphology and improved electrical
13 properties (20 - 30 Ω /sq. vs. 70-80 Ω /sq.) compared to commercially available ITO films grown
14 on PET by sputtering.

15 ITO films were deposited using silver foil as the flexible substrate using PLD. The
16 deposited films show a surface roughness that is comparable or better than the surface roughness
17 of the substrate. The RMS roughness of the silver foil substrate before the deposition of the ITO
18 film was 0.7 nm, and the RMS roughness of the film after deposition of the ITO film was also 0.7
19 nm.

20 ITO films were deposited using a thin silicon wafer as the flexible substrate using PLD.
21 The RMS roughness of the thin silicon wafer substrate before the deposition of the ITO film was
22 1.3 nm, and the RMS roughness of the film after deposition was also 1 nm.

1 Example 2

2 OLEDs were constructed using the transparent conducting films deposited by pulsed laser
3 deposition.

4 ITO thin films, deposited by PLD on PET substrates, were used as anode contacts in
5 organic light-emitting diodes (OLEDs). The performance of the device was measured. Fig. 7(a)
6 shows the OLED device configuration and Fig. 7(b) shows the chemical structures of the organic
7 materials used in this research. The device structure consists of a hole transport layer (HTL) 10,
8 of N, N'-diphenyl-N, N-bis (3-methylphenyl)1,1'-diphenyl-4,4'diamine (TPD), 50, and an electron
9 transport/emitting layer (ETL/EML) 20, of tris (8-hydroxyquinolinolato) aluminum (III) (Alq3),
10 60. The cathode contact 30, deposited on top of the ETL 20, is an alloy of Mg:Ag (ratio = 12:1 by
11 weight). Devices were fabricated by high vacuum vapor deposition, with a background pressure
12 of 1×10^{-7} Torr. ITO coated substrates 40, were cleaned by an oxygen plasma asher. After the
13 deposition of the organic layers, the Mg/Ag alloy was deposited through a shadow mask by
14 coevaporation from separate sources. The active emissive area of the device is approximately 2
15 mm x 2 mm. The current-voltage-luminance (I-V-L) data were taken in N₂ atmosphere using a
16 Keithley 238 current/voltage source and a luminance meter (Minolta LS-110).

17 Fig. 8 is a graph showing the characteristics of current density (J)-voltage (V) and
18 luminance (L)-voltage (V) output for OLEDs fabricated using a PLD ITO film on PET and using
19 a commercial ITO (supplied by Applied Films, USA) on glass. The thickness of both ITO films
20 was approximately 100 nm. The J-V curves show a typical diode behavior, with current and
21 luminance power output observed only in the forward bias. Fig. 8(a) is a graph that shows that a
22 current density of 100 A/m² was obtained at approximately 5.5 V for the PLD ITO/PET device

1 while the same current density was observed at a voltage of approximately 7.5 V for the
2 commercial ITO/glass device. Fig. 8(b) is a graph that shows that a luminance level of 1000
3 cd/m^2 is obtained at only 7 V in the device on PET, while the same value of luminance is
4 observed at 8.5 V for the device on glass. The reduction in the drive voltage and high luminance
5 efficiency make an ITO coated PET substrate very promising for future OLED application.

6 Although a few embodiments of the present invention have been shown and described, it
7 would be appreciated by those skilled in the art that changes may be made in these embodiments
8 without departing from the principles and spirit of the invention, the scope of which is defined in
9 the claims and their equivalents.

1 ABSTRACT

2

3 The invention relates to the deposition of transparent conducting thin films, such as transparent
4 conducting oxides (TCO) such as tin doped indium oxide (ITO) and aluminum doped zinc oxide
5 (AZO) on flexible substrates by pulsed laser deposition. The coated substrates are used to
6 construct low cost, lightweight, flexible displays based on organic light emitting diodes (OLEDs).

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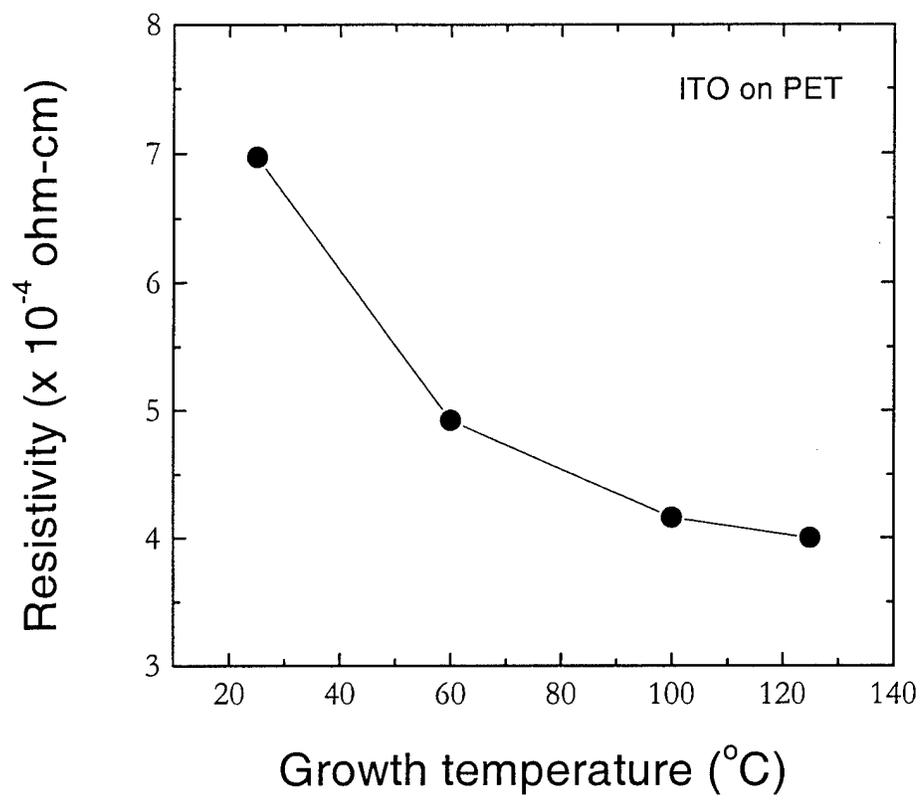


Fig. 1

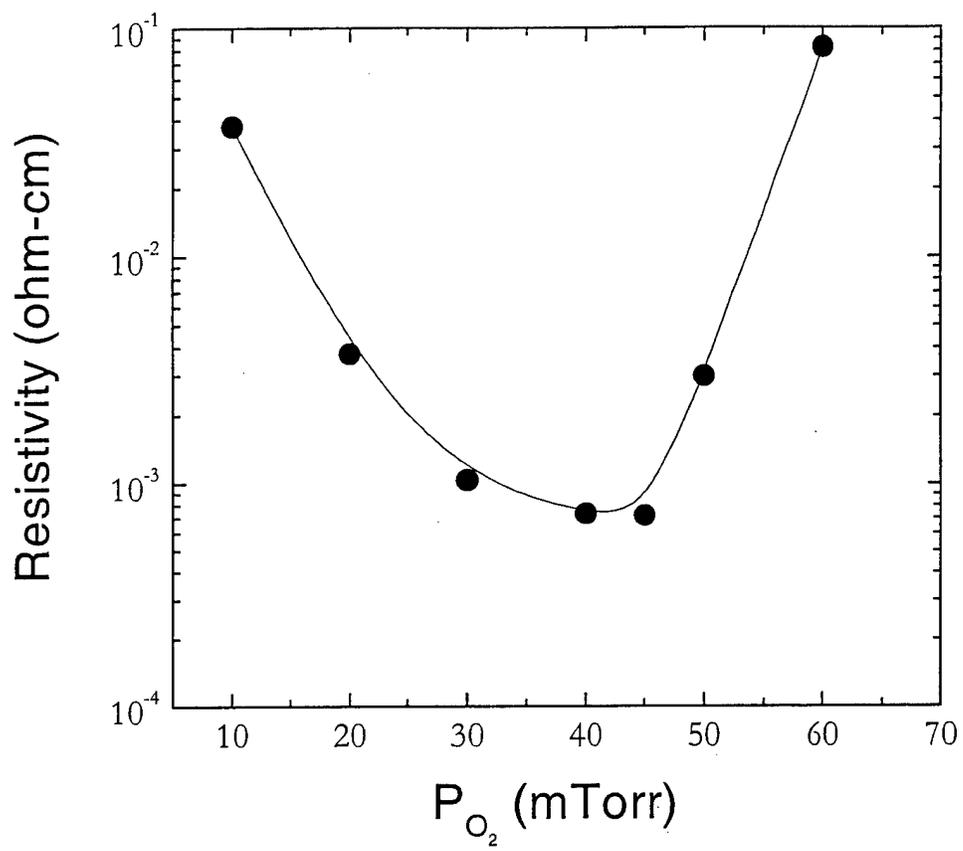


Fig. 2

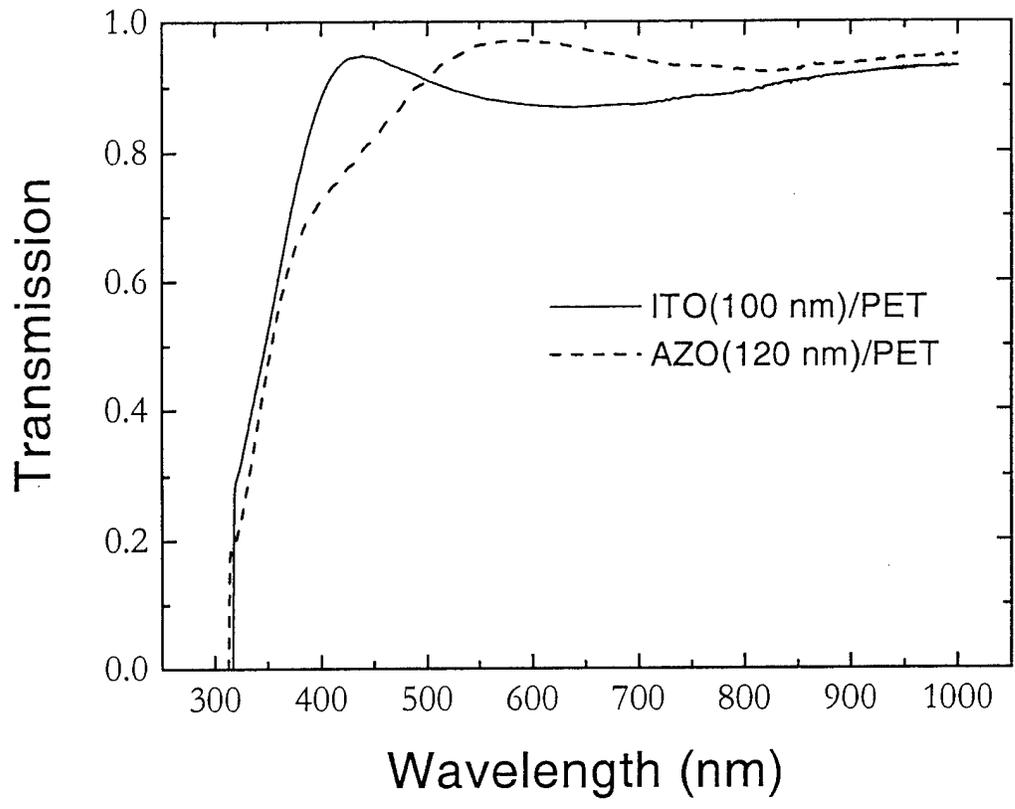


Fig. 3

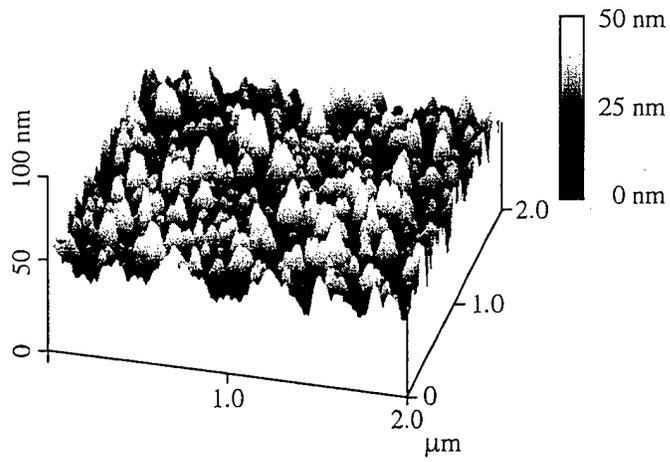


Fig. 4(a)

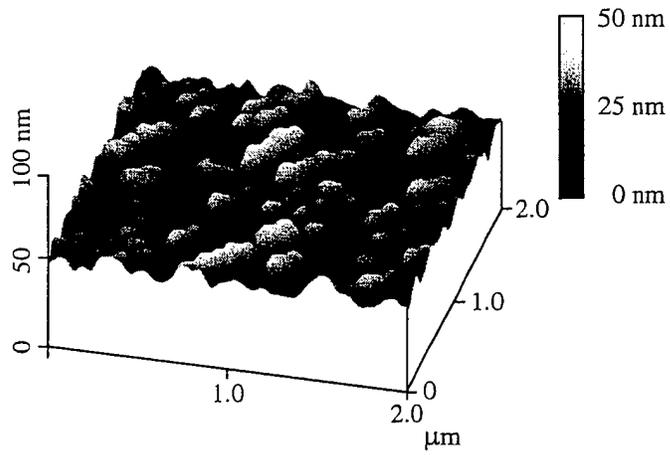


Fig. 4(b)

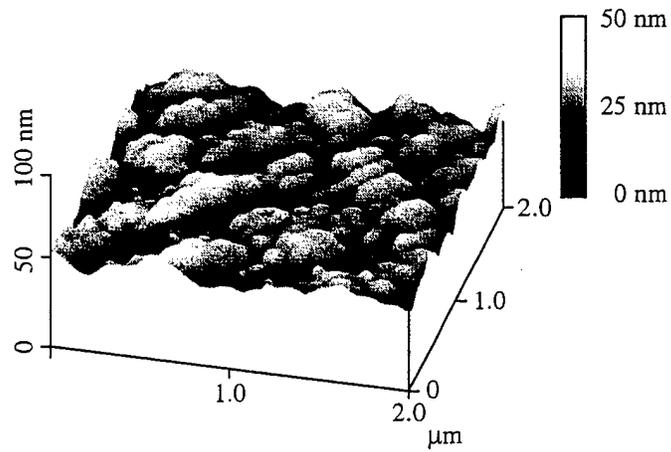


Fig. 4(c)

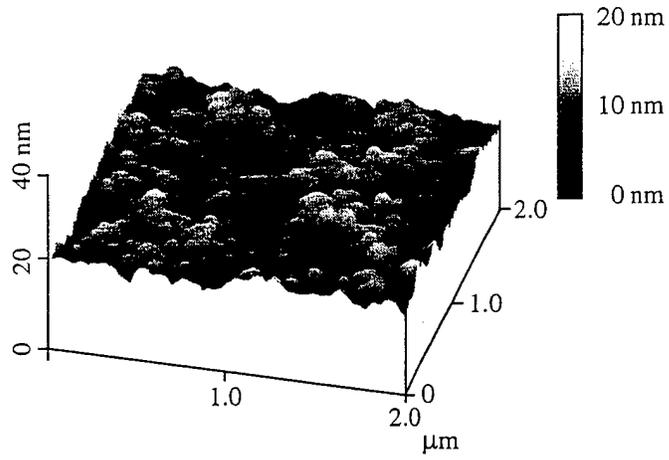


Fig. 5(a)

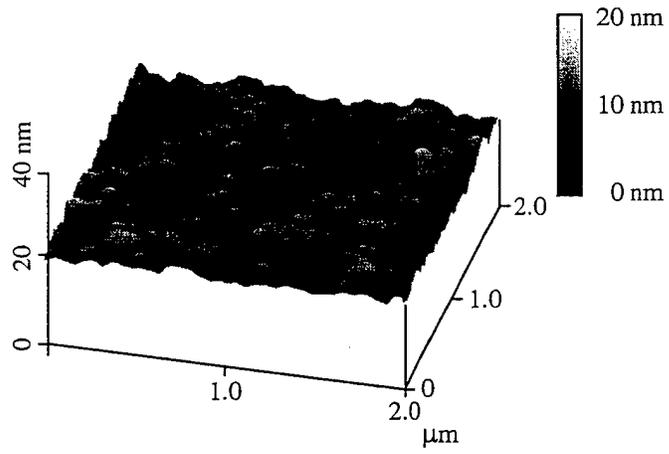


Fig. 5(b)

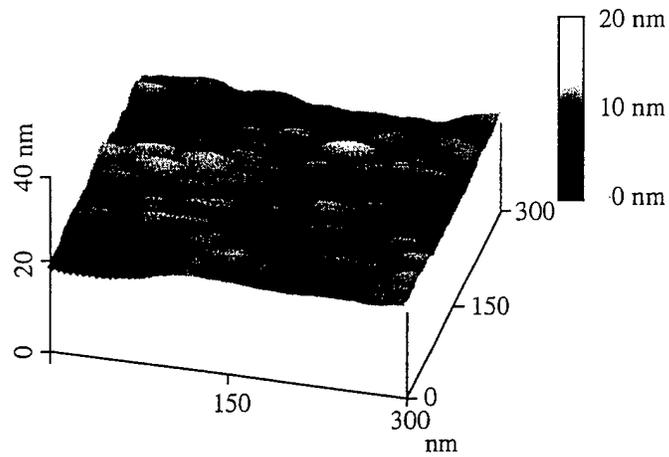


Fig.6(a)

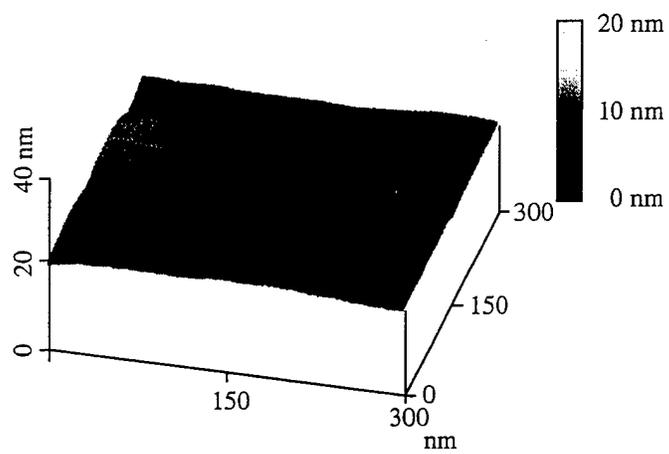


Fig. 6(b)

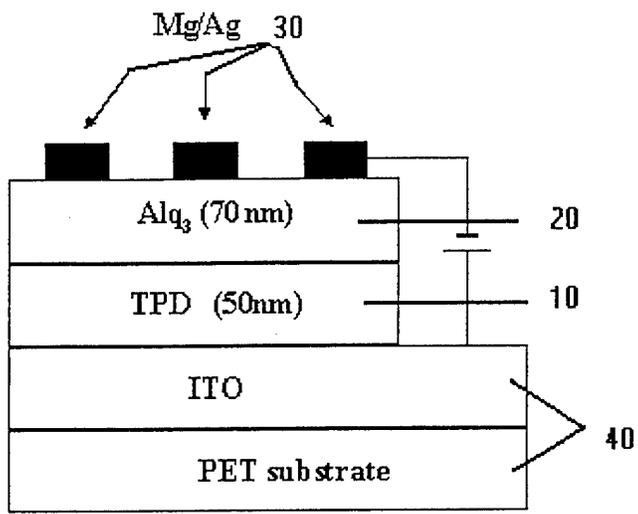


Fig. 7(a)

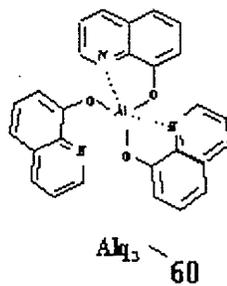
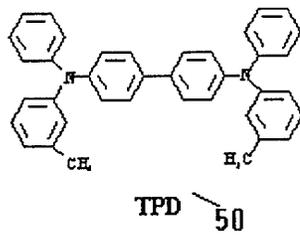


Fig. 7(b)

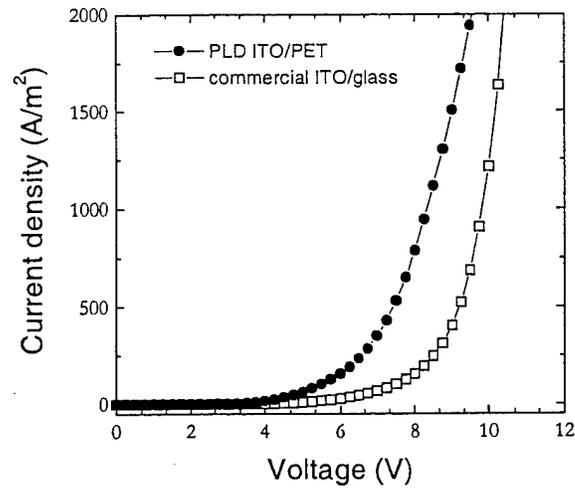


Fig. 8(a)

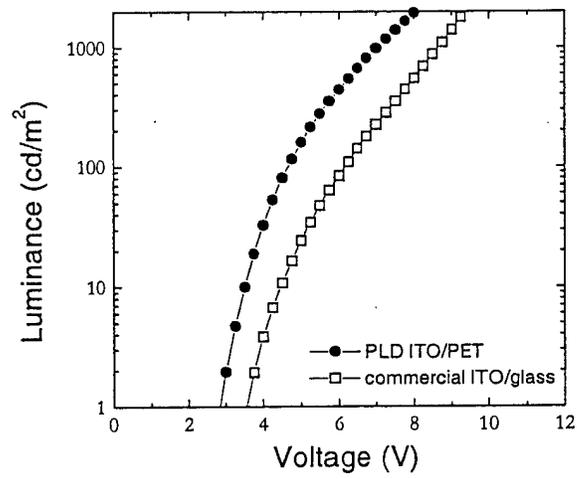


Fig. 8(b)