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Application of Thin Films of Polyaniline and Polypyrrole in Novel Light-Emitting Devices and Liquid Crystal Devices

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Light-emitting electroluminescent devices are described in which the conjugated light emitting polymer is separated from one or both of the device electrodes by a film of non-conducting polyaniline. Novel electrochemically-driven electroluminscent devices are also described. The effect on the properties of polypyrrole or polyaniline (deposited from aqueous polymerizing solutions of the monomer) caused by the hydrophilicity/hydrophobicity of the substrate surface is utilized by a "microcontact printing" technique to form patterned liquid crystal display devices.

The ability to cast high quality thin films of conducting polymers from their solutions in organic solvents (*1*,*2*) or to deposit them on selected substrates from aqueous solution (*3-5*) has permitted their use both in their lowly conducting (*6*) and also in their highly conducting forms (*7*) in novel devices. The non-doped semiconducting form of polyaniline (emeraldine base ; EB) can, for example, be conveniently spin-cast from its solution in N-methylpyrrolidinone (NMP) to produce high quality thin films (*4*,*5*). Thin cohesive films of polyaniline (*4*,*5*) and polypyrrole (*3*,*4*) in their doped, highly conducting form can readily be deposited on selected polymer or glass substrates by a "1-dip" *in situ* process from dilute aqueous solutions of the monomer where it is undergoing oxidative polymerization.

In this report, we describe the preparation and properties of certain types of the above films and their use in novel electroluminscent and liquid crystal display devices and in "microcontact printing".

Symmetrically Configured AC Light-Emitting (SCALE) Devices

Light-emitting "5-layer" devices having the configuration M/EB/P/EB/ITO when M=Al, Cu or Au, EB=polyaniline (emeraldine base), P=poly(2,5-dihexadecanoxy phenylene vinylene pyridyl vinylene), PPV.PPyV and ITO=indium tin oxide glass show electroluminescent properties in both forward and reverse bias modes (*6*,*8-9*) (Figures 1-3). Furthermore, as shown in Figure 2, the devices can operate with an AC applied potential; two light pulses are observed in each cycle. At appropriately

selected potentials, light emission in the forward bias mode is more intense when M=Al but is more intense in the reverse bias mode when M=Au. When M=Cu the intensities in the forward and reverse bias modes are approximately the same at ±~27 V. In the absence of the insulating emeraldine base, in the case of aluminum and copper, electroluminescence is observed only in the forward bias mode; in the case of gold no electroluminescence is observed in either forward or reverse bias modes.

In order to understand the role of EB, the following devices involving only aluminum were constructed in which the position and the number of layers of EB were varied from zero to one to two, viz., "3-layers":Al/PPV.PPyV/ITO; "4-layers-1": Al/PPV.PPyV/EB/ITO; "4-layers-2": Al/EB/PPV.PPyV/ITO; "5-layers": Al/EB/PPV.PPyV/EB/ITO. The corresponding I/V curves are given in Figure 4. Only the SCALE ("5-layers") device shows the capability of operating in both forward and reverse bias modes and in an AC mode. In the "5-layers" device only, both holes and electrons can be injected from both ITO glass and from Al electrodes. A similar phenomenon is observed when copper is used instead of aluminum in analogous "3-layers" and "5-layers" devices. As can be seen, these devices exhibit most unusual electrical properties, viz., as the number of insulating layers *increases*, the total resistance of the device at a given potential *decreases*.

Unless the electrical properties of light emiting devices are first understood it seems most unlikely that their electroluminescent properties, which are dependent on the electrical properties, can be completely understood. The possibility must be considered that under appropriate conditions, EB might act both as a good electron and as a good hole transporting material. It may be concluded that reduction in injection barriers for electrons or holes may possibly be optimized by judicious matching of electrode material which interacts chemically in a favorable manner with the polymer with which it is in contact and that the nature of the polymer/polymer interface may also play a critical role.

Electrochemically-Driven Light-Emitting Cells

Electrochemically-driven light-emitting cells have been reported very recently although there is not yet complete agreement as to the exact mechanism or processes by which they operate (*10-14*). It appears that a p/n junction is initially formed (by electrochemical p- and n- doping of a conjugated emissive polymer) in the center of a thin film of the conjugated polymer containing a solid electrolyte such as $LiCF_3SO_3$ dissolved in polyethylene oxide, PEO, sandwiched between two electrodes. It is postulated (*10-12*) that the small turn-on potentials observed (approximately equal to the energy band gap of the emissive polymer) are due to the fact that the dopant anions and cations associated with the p- and n- doping processes respectively, compensate for the charges on the polymer chains. This may be compared with a conventional LED in which the semiconducting emissive polymer layer is oxidized on one side (holes are injected) and reduced on the other (electrons are injected) but in which no doping (injection of counter dopant ions) is involved. The electrons and holes are injected by tunneling through the energy barriers formed at the electrode/polymer interfaces.

It has been stated (*12*) that if the PEO is eliminated from a Al/PPV;$LiCF_3SO_3$;PEO/ITO cell where PPV=poly(*p*-phenylene vinylene) that it behaves similarly to the conventional Al/PPV/ITO LED device. However, we find that in an Al/MEH-PPV;TBATS/ITO cell (*15*) where TBATS=tetrabutylammonium p-toluenesulfonate (Figure 5) that it behaves very differently from an Al/MEH-PPV/ITO device (Figure 6). In particular, the presence of TBATS: (i) involves light-emission in the reverse bias mode, (ii) results in a much greater light intensity

clearly visible in the presence of a direct overhead fluorescent light, (iii) results in a lower turn on voltage and (iv) that in some, but not all devices, the current is in the microampere range rather than in the milliampere range normally associated with a conventional LED. We by no means pretend to understand at the present time the relative importance of the many possible variable parameters involved, but we believe that such devices are of very great scientific interest and of potential technological importance.

"1-Dip" *in situ* Deposition of Polypyrrole and Polyaniline on Hydrophobic and Hydrophilic Glass Surfaces.

High quality thin films of doped polypyrrole and doped polyaniline can be conveniently deposited during a few minutes at room temperature on glass and plastic substrates from dilute aqueous solutions of the respective monomer as it undergoes oxidative polymerization (*3-5,15*). We find that the deposition rate and the properties of the films are greatly dependent on the nature of the substrate surface, e.g., whether deposited on hydrophilic or hydrophobic surfaces.

Glass microscope slides may be readily rendered hydrophilic (advancing water contact angle $< \sim 5^0$) by treatment with a hot concentrated sulfuric acid/30% hydrogen peroxide mixture or hydrophobic (advancing water contact angle $\sim 110^0$) by a standard treatment involving exposure to ~ 0.4 wt% hexane solution of $C_{18}H_{37}SiCl_3$.

Figures 7 and 8 show the result of deposition studies involving polypyrrole (*15*) and polyaniline respectively in which treated glass microscope slides were dipped in the same solution of polymerizing monomer for the same length of time. In both cases the rate of deposition of polymer on the hydrophobic surface is very much greater than on the hydrophilic surface. We believe that this may be related to the "like dissolves like" principle, i.e., some of the covalent monomer is preferentially adsorbed from the aqueous solution on to the covalent $C_{18}H_{37}$- film coating the surface more so than on to the polar hydrophilic glass surface, thus favoring more rapid polymerization on the hydrophobic surface. For both polymers, adhesion is stronger to the hydrophilic surface, the films passing the "Scotch Tape" test.

Not surprisingly, the surface resistance of the thinner films on the hydrophilic surfaces is very much greater than that of the thicker films deposited on the hydrophobic surfaces. It is also possible that the conductivity of the films deposited on the hydrophilic and hydrophobic surfaces may differ from each other. This possibility is presently being investigated.

As can be seen from Figure 7, the spectra of the polypyrrole films deposited on hydrophilic and hydrophobic surfaces differ greatly, the peak at 1182 nm for example in the former spectrum being absent in the latter spectrum which instead shows a well defined free carrier tail extending to 2600 nm. By analogy with studies on polyaniline (*16*), we believe that the polymer deposited on the hydrophilic surface might have a tight coil molecular conformation while that deposited on the hydrophobic surface might have an expanded coil molecular conformation.

It can be seen from Figure 8 that the spectra of the polyaniline films differ, although not as greatly as for the polypyrrole films, according to whether it is deposited on hydrophilic or hydrophobic surfaces. It should be noted that different dopant anions were used for the polypyrrole and polyaniline films. On-going studies suggest that the two polymers may behave even more similarly when they both have the same dopant anion.

Flexible Liquid Crystal "Light Valves"

Novel, flexible, completely organic, polymer dispersed liquid crystal (PDLC) "light valves" were fabricated using two flat pieces of commercial overhead transparency substrates (Nashua *xf-20*) coated with polypyrrole between which a film of commercial PDLC material (Norland Products Co. NOA 65 optical adhesive and BDH Ltd. E7 liquid crystal fluid together with EM. Ind. 15 micron polystyrene spacers) was sandwiched. The optical adhesive was polymerized by exposure to UV light. Thin conducting polypyrrole films of varying controllable thickness were deposited on the overhead transparency.

For use in flat screen liquid crystal displays it is necessary to optimize the thickness of the polypyrrole deposit so as to simultaneously obtain the maximum transmittance and minimum resistance necessary for satisfactory devices. For example, a 10 minute dip of Nashua *xf-20* overhead transparency produces a polypyrrole film having a thickness of ~250 angstroms, a surface resistivity of 7,200 ohms/square and a transmittance centered near the middle (600 nm) of the visible region (~400 nm to ~800 nm) of 89% using an uncoated substrate in the reference beam of the spectrometer. Figure 9 illustrates preliminary results obtained to date with a completely flexible, all organic light valve using polypyrrole as the conducting medium for both electrodes (*17*). A PDLC device using conducting ITO glass for both electrodes was used as a standard for comparison. The results are satisfactory for certain applications such as light-weight, non-breakable windows of variable transmittance.

Application of "Microcontact Printing" for the Production of Patterned Polypyrrole and Polyaniline Films

We are combining the selective deposition of polypyrrole and polyaniline on hydrophilic/hydrophobic surfaces as described in the preceeding section with the recent microcontact printing technique (*18-20*) to produce patterned conducting polymer films which we have demonstrated can be used in PDLC display-type devices.

A key objective of the collaborative research with G. M. Whitesides and Y. Xia (Harvard University) is to determine the maximum resolution of polyaniline and polypyrrole patterns attainable using only simple, commonly available equipment, i.e., a desk-top computer and a standard spectrometer plotter, (resolution, ~ 25 um). The steps comprise: (i) designing any desired pattern on the computer, (ii) reducing the pattern on the computer to any desired size, e.g. > ~ 1 cm x 1cm; (iii) transferring the design to a floppy disk, (iv) inserting the disk into the computer driving the plotter of the spectrometer, (v) replacing the pen in the plotter by an object with a sharp point, e.g. a sewing needle, (vi) covering , e.g. by spinning or other means a heated microscope slide or silicon wafer with a thin layer (~ 20-40 um) of low melting (working temperature ~ 52^0C) wax such as Amaco Flexwax 120, (vii) scratching the pattern on the thin layer of wax using the needle in the pen holder of the plotter, and placing it (attached to its substrate) in a petri dish, (viii) pouring a well stirred mixture of Dow Corning Sylgard 184 silicone elastomer (10 parts by weight) and Sylgard 184 curing agent (1 part by weight) on top of the wax engraving to a depth of 5-10 mm, (ix) allowing the mixture to polymerize to the silicone elastomer during ~ 3 days at room temperature, (x) removing the silicone stamp from the wax-engraved pattern and discarding (it has the wax "scrapings" produced in the engraving of the pattern adhering to it, (xi) repeating step (viii) and allowing polymerization , (xii) removing the silicone elastomeric stamp which now has the 3-D design imprinted on its lower face, (xiii) wiping the patterned face of the silicone stamp with a piece of cotton containing the "ink" as a ~ 0.4 wt% solution of $C_{18}H_{37}SiCl_3$ in n-hexane, (xiv) evaporating the n-hexane in a stream of nitrogen for

~ 1min., (xv) pressing the stamp firmly for ~ 10 seconds on the substrate surface so as to imprint a pattern of a thin hydrophobic $C_{18}H_{37}$- film on the substrate, (xvi) immediately cleaning the stamp by rinsing it with cotton soaked in n-hexane, (xvii) placing the substrate having the imprinted $C_{18}H_{37}$- layer in to the appropriate dipping solution.

An example of an SEM of polyaniline.HCl selectively *in situ*-deposited (5.5 min. dipping time) on an ~ 100 um wide hydrophobic $C_{18}H_{37}$- line imprinted on a clean , hydrophilic microscope slide is given in Figure 10.

Examples of the selectivity of polypyrrole 1-dip, *in situ*, deposition are given in the SEMs in Figure 11. Dark lines are polypyrrole selectively deposited on hydrophobic $C_{18}H_{37}$- surfaces imprinted on a clean, hydrophilic microscope slide as substrate. The upper three figures (Figures 11a) originated from a desk-top computer-drawn pattern used for producing the wax engraved master; the deposition time in the polymerizing pyrrole solution was 12.0 min. Preliminary studies directed towards optimizing both the selectivity of deposition and resolution using the wax engraving technique are very encouraging. The lower two figures (Figures 11b) demonstrate the resolution attainable using a commercial relief master from which the silicone stamp was made. Our objective is to attain these types of results using the (non-lithographic) wax engraving technique. Since the silicone stamps can be used repeatedly without loss of resolution (*18-19*), this technique holds potential promise for the inexpensive production of semi-micro circuitry and liquid crystal displays on rigid or flexible substrates in certain types of "throw away" devices such as, e.g., sensors.

As an example, an effective polymer dispersed liquid crystal interdigitated array display has been fabricated by combining the concepts and techniques given in the "Flexible Liquid Crystal Light Valves" section with those given in this section. A thin interdigitated polypyrrole display pattern was deposited on a glass microscope slide as described above from the computer designed pattern given in Figure 12. Its thickness was chosen so that its optical transmittance and surface resistance were appropriate for liquid crystal display purposes. The PDLC mixture was sandwiched between the microscope slide (the polypyrrole pattern acting as one electrode) and ITO coated glass which acted as the other electrode. When placed on an overhead projector, the whole device produced a dark image on the screen. Application of an AC potential to the ITO/glass electrodes and one half of the pattern, produced a clear bright image of that half of the pattern, strong light passing through the semi-transparent polypyrrole line electrodes. Application of the potential to both polypyrrole electrodes resulted in both halves of the interdigitated polypyrrole array appearing as a white pattern on a black background on the projector screen. This dramatically demonstrates the large difference in surface resistance between polypyrrole deposited on hydrophobic vs. hydrophilic surfaces as described in Figure 7.

Conclusions

It is concluded that thin films of conducting polymers such as polyaniline and polypyrrole, whether in their highly or lowly conducting forms, whether cast from their solutions in organic solvents or deposited from solutions of the polymerizing monomer are of both fundamental scientific interest and of possible technological use for certain applications. However, much still remains to be understood concerning the role of conjugated polymers in various light-emitting devices and the effect on their properties induced by the nature of the substrate surface on which they are deposited.

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Figure 1. I-V characteristics of SCALE devices using (A) Al, (B) Cu and (C) Au as the electrode.

Figure 2. Electroluminescence intensity as a function of time for a metal/EB/PPV.PPyV/EB/ITO device driven by a 1 Hz sinusoidal voltage: metal (a) Al from ± 8 V, (b) Cu from ± 27 V and (c) Au from ± 8 V.

Figure 3. Electroluminescent spectra of a Au/EB/PPV.PPyV/EB/ITO device in forward and reverse bias modes at ~ ± 8 V. For clarity, the intensity in the forward mode (λ_{max} = 585 nm) has been normalized to approximately the same intensity as in the reverse bias mode (λ_{max} = 616 nm).

Figure 4. I-V characteristics of 3-layered, 4-layered and 5-layered devices.

Figure 5. Current density and intensity of light emission vs. voltage in a Al/MEH-PPV+TBATS/ITO device.

Figure 6. I-V characteristics of a Al/MEH-PPV/ITO device.

Figure 7. Vis/uv spectra of polypyrrole anthraquinone-2-sulfonate deposited (dipping time: 15 minutes) on (A) a hydrophobic glass surface (film thickness ~ 400 Å) and (B) a hydrophilic glass surface. (Spectrum A was recorded vs. a hydrophobic glass slide in the spectrometer reference beam and spectrum B was recorded vs. a hydrophilic glass slide in the spectrometer reference beam).

Figure 8. Vis/uv spectra of polyaniline.HCl deposited (dipping time: 5.5 minutes) on (A) a hydrophobic glass surface (film thickness ~ 1200 Å) and (B) a hydrophilic glass surface. (Both spectra were recorded vs. "as-received" glass microscope slides in the spectrometer reference beam).

Figure 9. Relationship between transparency (% transmittance in air at 600 nm) and applied voltage of polymer dispersed liquid crystal display devices constructed using two ITO glass electrodes and two polypyrrole film (on plastic) electrodes as the conducting transparent substrates.

Figure 10. SEM of polyaniline.HCl selectively deposited by a "1-dip" process on a ~100 μm wide line of hydrophobic $C_{18}H_{37}SiCl_3$ substrate.

Figure 11. Selective deposition of polypyrrole on patterned hydrophobic surface.

Figure 12. Computer constructed and computer reduced (17mm x 17mm) interdigitated array.

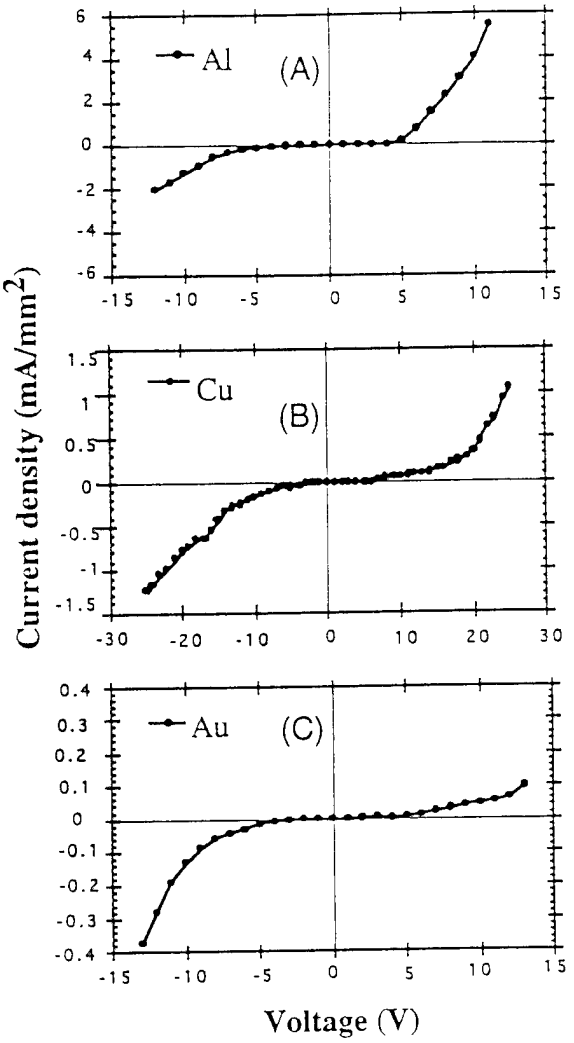
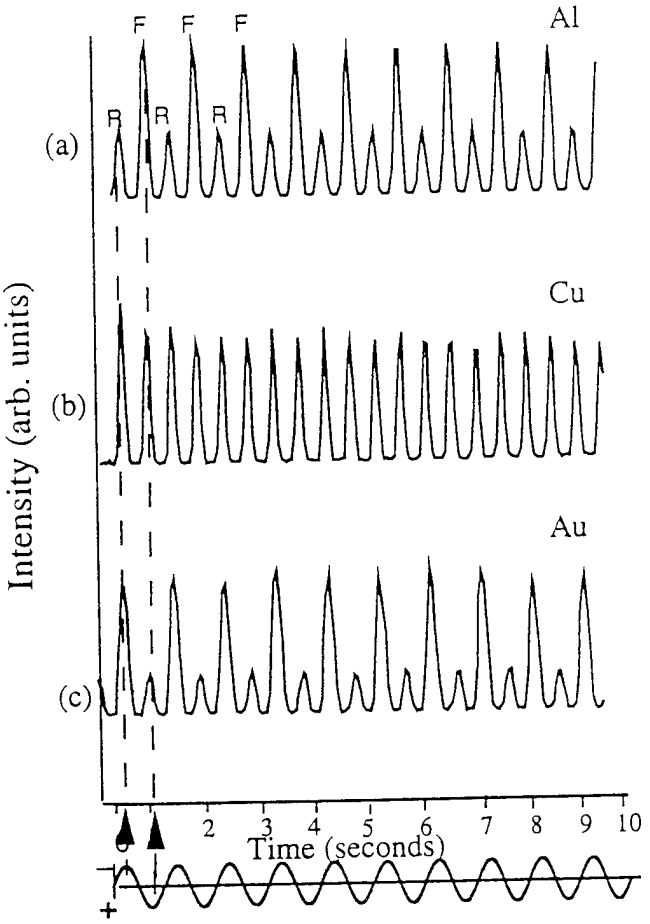


FIG. 1

FIG. 1


F F F
R R R
Al
Cu
Au
(a)
(b)
(c)
Intensity (arb. units)
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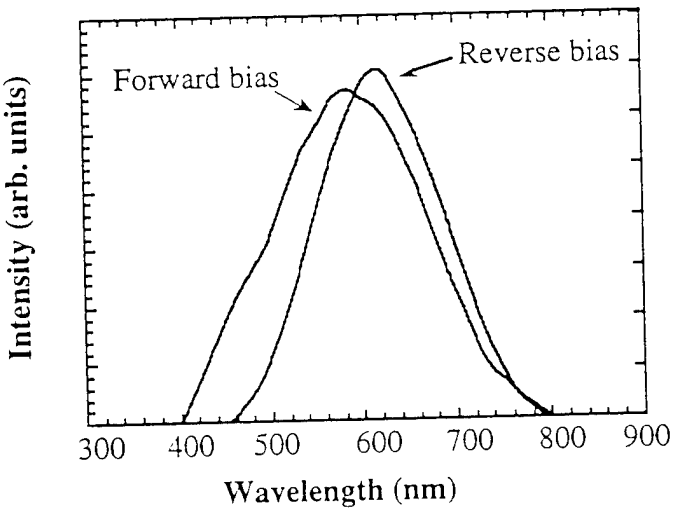
Time (seconds)
e
+

FIG. 2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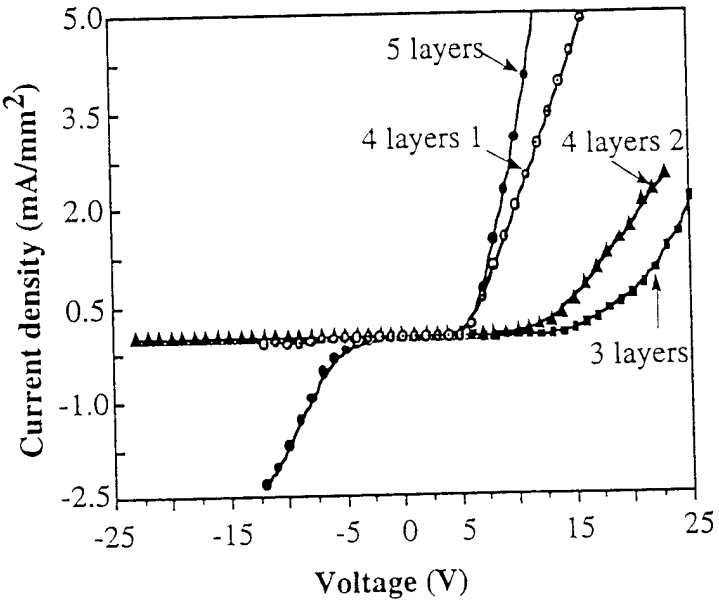
700
800
900
Wavelength (nm)

FIG. 3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0.5
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-2.5
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-5
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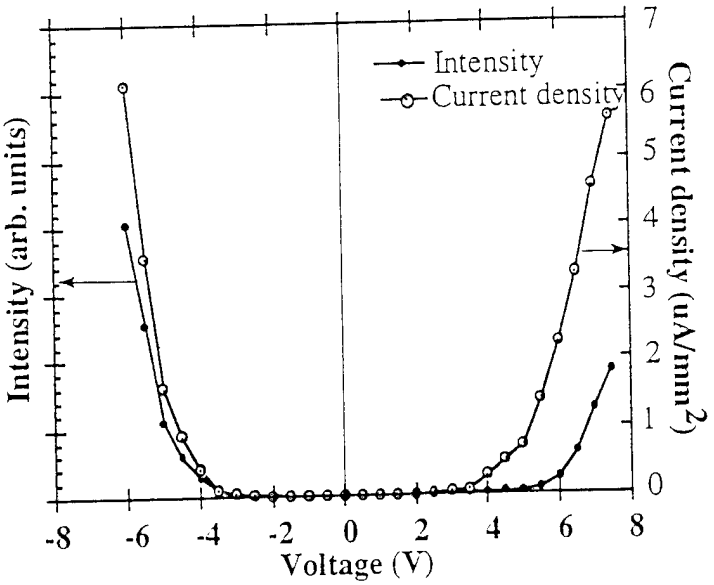
5
15
25
Voltage (V)
5 layers
4 layers 1
4 layers 2
3 layers

FIG. 4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Current density
Intensity (arb. units)
Current density (uA/mm2)
Voltage (V)
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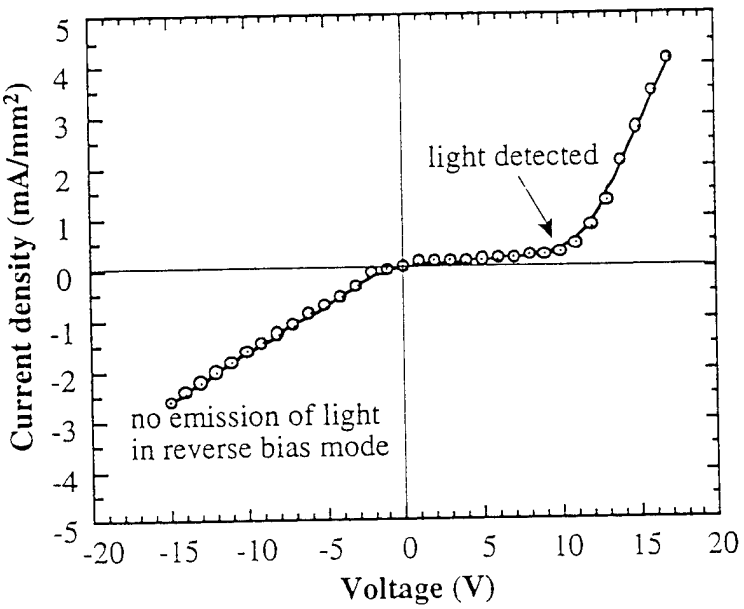
7

FIG. 5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-2
-3
-4
-5
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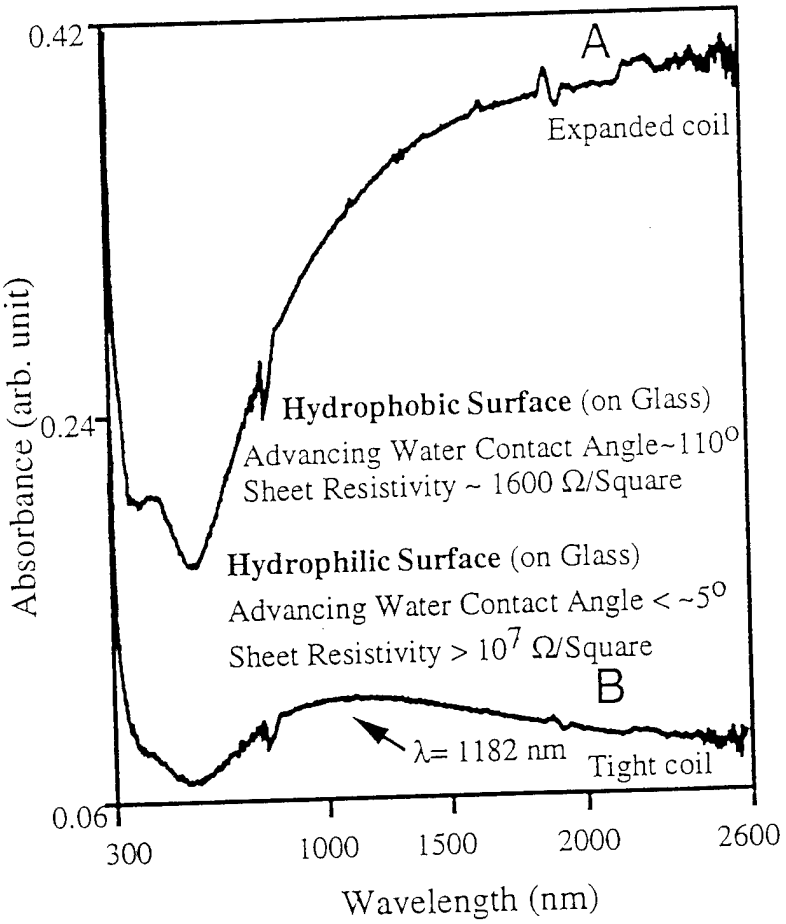
-15
-10
-5
0
5
10
15
20
Voltage (V)
light detected
no emission of light
in reverse bias mode

FIG. 6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0.06
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Advancing Water Contact Angle~110°
Sheet Resistivity ~ 1600 Ω/Square
Hydrophilic Surface (on Glass)
Advancing Water Contact Angle < ~5°
Sheet Resistivity > 10^7 Ω/Square
B
λ= 1182 nm
Tight coil
300
1000
1500
2000
2600
Wavelength (nm)

FIG. 7

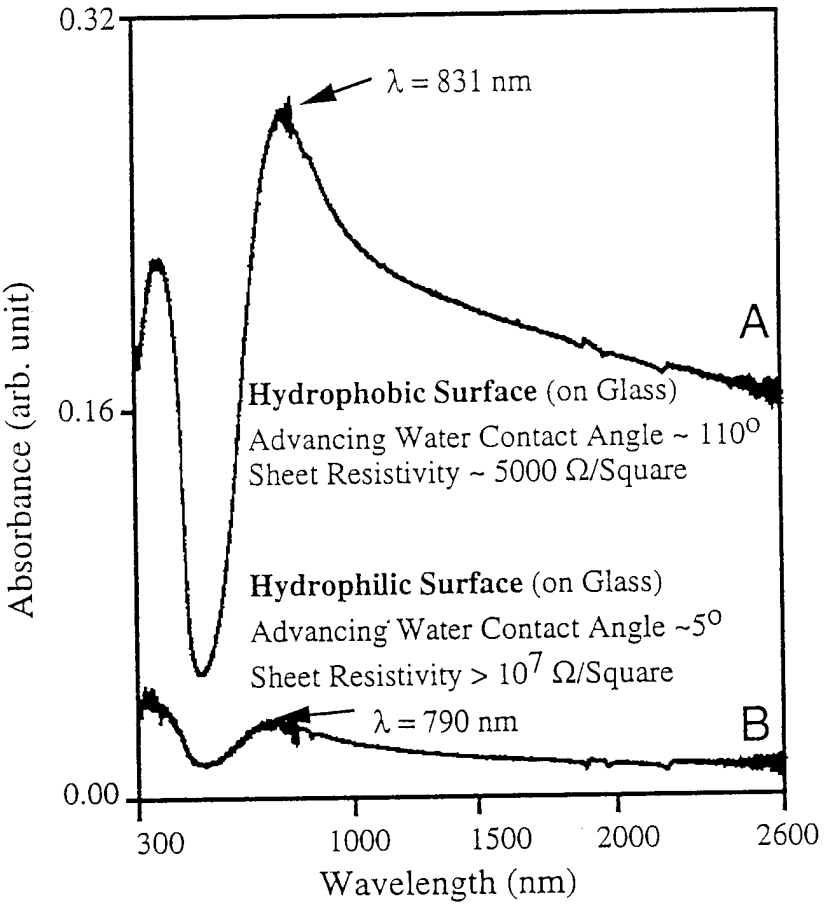

0.32
0.16
0.00
Absorbance (arb. unit)
λ = 831 nm
A
Hydrophobic Surface (on Glass)
Advancing Water Contact Angle ~ 110°
Sheet Resistivity ~ 5000 Ω/Square
Hydrophilic Surface (on Glass)
Advancing Water Contact Angle ~5°
Sheet Resistivity > 10^7 Ω/Square
λ = 790 nm
B
300
1000
1500
2000
2600
Wavelength (nm)

FIG. 8

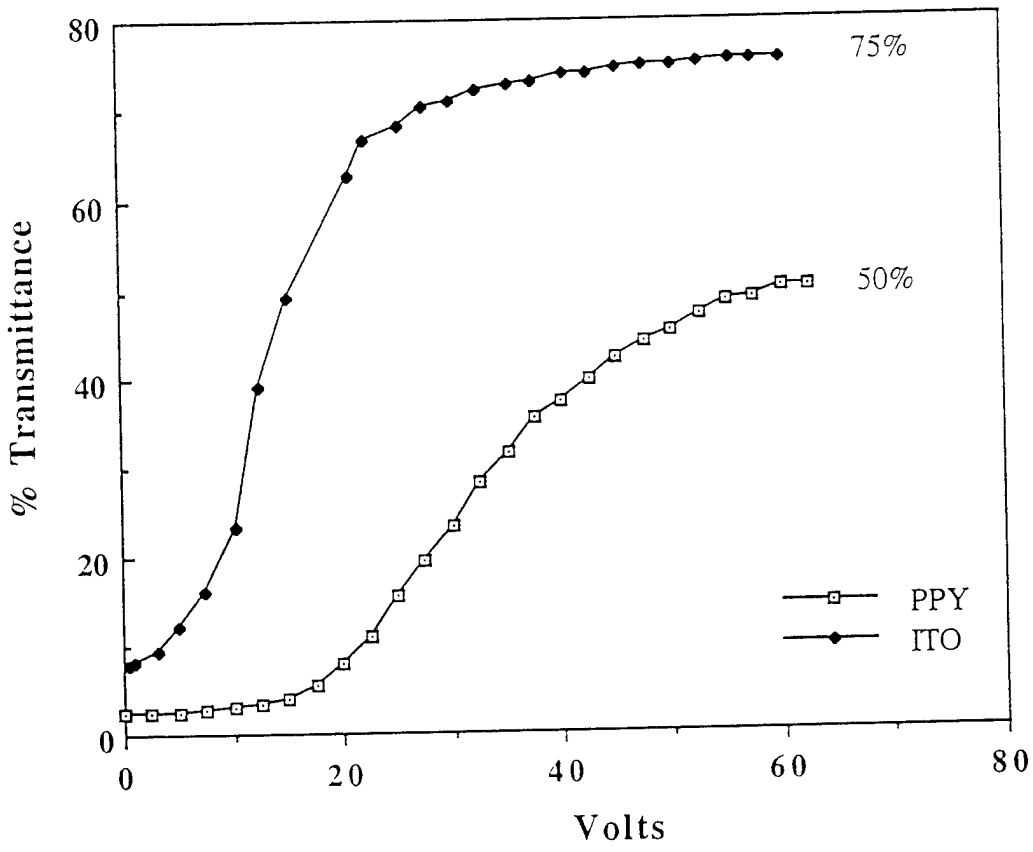


FIG. 9

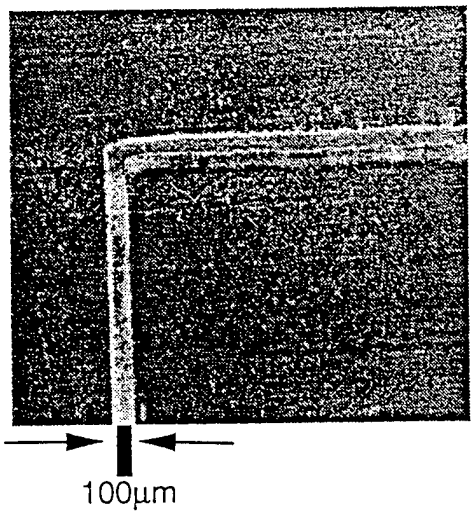


FIG. 10

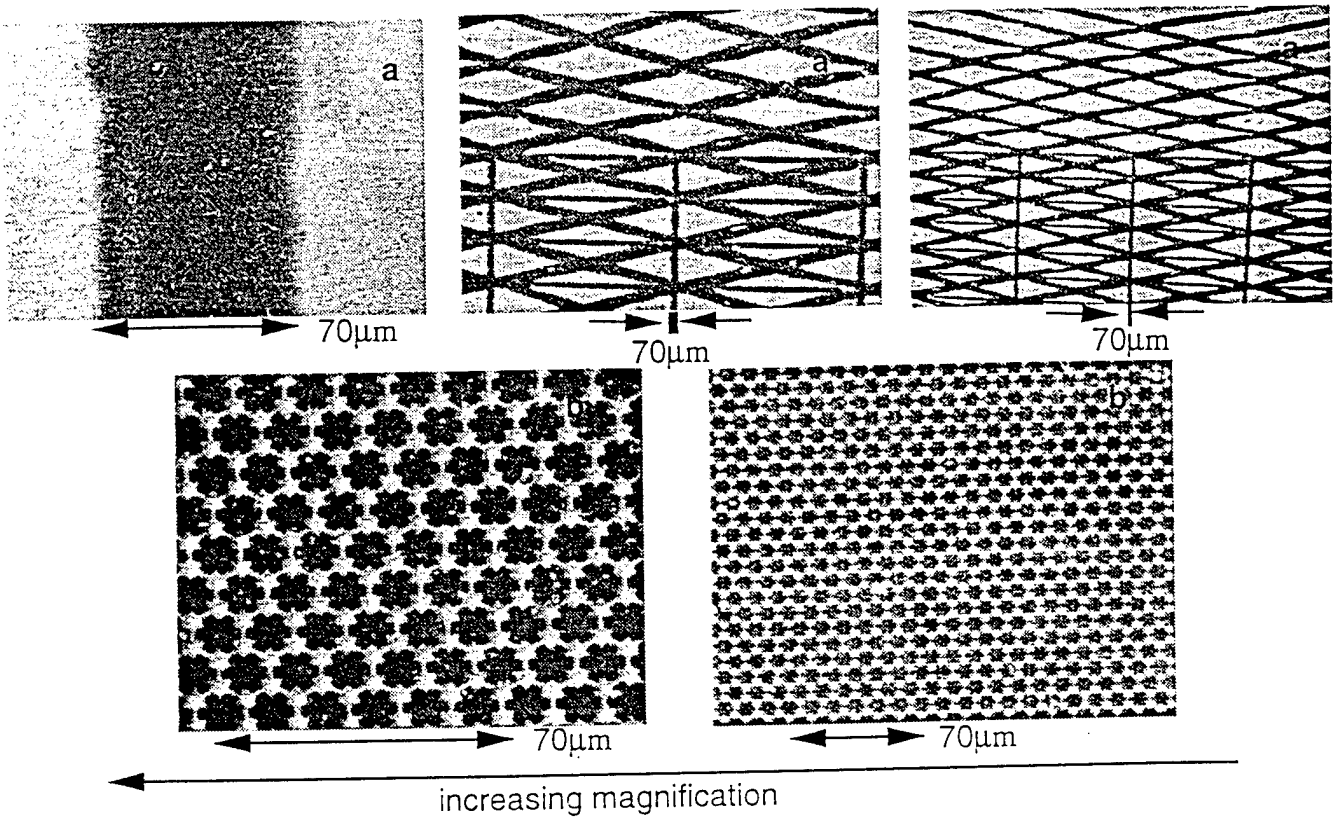
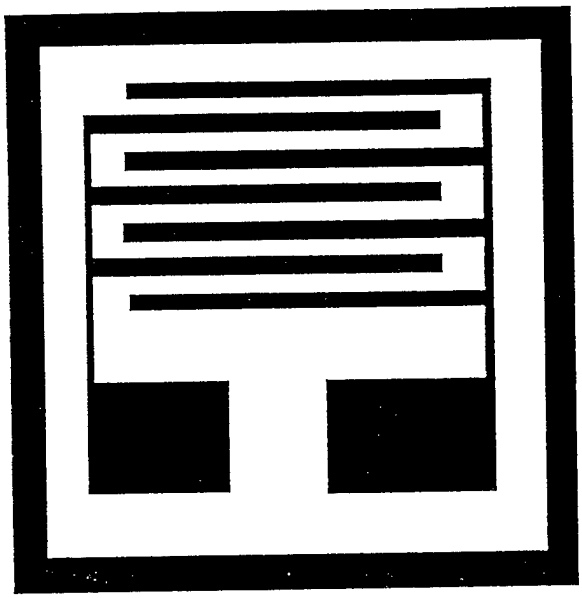


FIG. 11



Size
reduction

Interdigitated pattern
designed on computer

FIG. 12