Process Spotlight: ITO Etching, Part I

Indium tin oxide (ITO) is the primary transparent conductive oxide (TCO) used in flat panel displays. Passive matrix LCDs typically use ITO exclusively as display electrodes; active matrix LCDs use unpatterned ITO on the color filter plate, and patterned ITO in the viewable aperture of each subpixel on the TFT plate. Patterning ITO is usually accomplished by wet etching methods, but can be done with dry etch processes as well.

Despite concerns about a worldwide indium shortage (see references below), ITO continues to dominate the market. Alternative TCOs such as AZO, zinc oxide, and nanoparticle-type films such as carbon nanotubes or Cambrios Technologies’ TCF offer some advantages but have not yet made much of a dent into ITO usage for displays.

Standard ITO films are primarily indium oxide (In2O3) doped with tin. The indium/tin ratio is usually 90/10. Most ITO is now deposited by pulsed DC sputtering of an ITO target. Before this, ITO was deposited either by reactive DC sputtering of an In/Sn target, or by RF sputtering of an ITO target. Either method was prone to formation of spikes in the film, which made fine patterning and thin cell gaps difficult to achieve without shorting. Today ITO films have extremely good uniformity and flatness, suitable even for OLED applications. Sheet resistances of less than 100 ohms per square can be achieved with extremely thin films, 20 nanometers or less in many cases.

ITO films are usually patterned with standard photolithographic methods and wet etching. Positive or negative photoresist materials can be used. The mechanism of ITO etching is somewhat complicated, but typically centers around hydrochloric acid, usually in combination with an oxidizing agent. Many recipes call for heating of the etchant to 40-50°C to increase etch rates (etch rate is exponential with temperature).

A few specific ITO etch bath recipes:
1. HCl / HNO3. Mix concentrated HCl (37%) 1:1 with DI water; then add 5% nitric to this solution. Source: Donnelly / Applied Films Corp. (ITO coating vendor)
2. 6M HCl + 0.2M FeCl3. (source 1 below)
3. FeCl3 / HCl. 25% FeCl3, 1-5% HCl (source Transene Corporation)
4. HCl / CuSO4. 1000ml H2O + 980ml HCL (50%) + 3 tsp. Cupric Sulfate (source an ITO coating vendor)

Scholten (reference 1 below) has shown that a halogen acid such as HCl will etch ITO, but that it is the undissociated HCl molecule (rather than H+ or Cl-) that is responsible for the etching. In particular, HCl attacks the In-O bonds, resulting in an In-OH bond and an In-Cl bond. The next HCl molecule can then
attack the remaining In-OH bond, leaving In-Cl and H2O. Addition of an oxidizing agent will enhance
the etch rate, and give sharper features, as opposed to the somewhat jagged edges of pure HCl etching.

Scholten explained the mechanism for this enhancement by showing that strong oxidizers could
delocalize the In-OH intermediate, and in some cases remove an electron, resulting in radical OH. The In
site would retain a positive charge, and could react with a Cl- ion, resulting in an In-Cl bond. The
presence of the oxidizing agent rapidly consumes these In-OH intermediates, resulting in faster etching
(depending upon the strength of the oxidizing agent). Without this, the intermediates can move (they will
have some surface mobility to hop to neighboring molecules) and etching can become more “ragged” in
appearance. SEM images from Scholten show this effect on a submicron scale quite nicely.

The LCDRF uses a standard HCl / HNO3 bath to etch ITO, but is investigating FeCl3 as well. Features
as small as 3 microns have been patterned using the Oriel Mask Aligner and wet etching. If you are
interested in learning more about the ITO patterning capabilities of the LCDRF, please contact Doug
Bryant.

Next month we will discuss how to etch micron scale features in ITO, and dry etching methods.

Some resources to learn more about ITO etching:

Info on indium “shortages”:
http://www.indium.com/supply.php (Indium metal vendor statement on supply)
“What’s Next: Heavy Metal Alternatives”, in Pro AV Magazine, 2004:
http://proav.pubdyn.com/Tech_Apps/16-ProAV-Old%20Site%20Content-2004-410-
410proavwhatsnext.htm
“Almost Magical Metal in Short Supply”, Evan Ramstad, Wall Street Journal, August 10, 2004

Wet etching of ITO:
http://scitation.aip.org/getabs/servlet/GetabsServlet?prog=normal&id=JESOAN0001420000700232100
001&idtype=cvips&gifs=yes
http://scitation.aip.org/getabs/servlet/GetabsServlet?prog=normal&id=JESOAN000140000020047100
001&idtype=cvips&gifs=yes
3. “Microstructure and etching properties of sputtered indium - tin oxide (ITO) “, M. Hoheisel, C.
4. “On the homogeneity of sputter-deposited ITO films Part II. Etching behaviour”, van den Meerakker et

Equipment Update
Several tools in the LCDRF will be undergoing maintenance and upgrades, or have recently completed
maintenance:

Dr. Qihuo Wei’s Oxford 80+ reactive ion etcher (RIE) system was installed early in October. An
Oxford engineer will return in a few weeks for process training. Standard processes on this tool will be
etching of Si, SiO2, and silicon nitrides. Other processes are possible using the SF6 and CHF3 gases
(along with Ar or O2).
The **GenVac SC1 Coater** will undergo repair and upgrade in the coming weeks. New shielding has been designed to make system cleaning easier (in combination with the new blasting cabinet), and the ion gun will be repaired. This should restore ITO deposition capabilities in the near future. Deposition of aluminum, chrome, gold, and SiO2 are currently available.

The **Oriel Mask Aligner** will undergo lamp replacement / alignment and stage planarization later this month. This should improve performance with high resolution photolithography.

The **Technics PlanarEtch II** plasma etcher is currently down. No work is planned on this machine in the next month. If you have interest in using this machine, please contact Doug Bryant; if there is a need for it, we can bump this up in priority.

Nick Diorio, a first year graduate student in Chemical Physics who is working in the cleanroom this semester, has configured the **JA Woollam Co Spectroscopic Ellipsometer** so that routine thickness and index measurements can be done easily. The user does not need to know details about ellipsometry, or set up the measurement; he/she only needs to mount a coated silicon wafer and begin the measurement.

The **Quartz X One EDX** system mounted to the **Hitachi S2600-N SEM** has been recalibrated recently. This will allow for more accurate peak identification, and use of the mapping feature. Stricter guidelines are being drafted for users so that peak performance can be achieved in all cases. Some recent users had complained about excessive detector noise and broadened peaks—this should be taken care of at this point.

**Thin film characterization: Ellipsometry**

Over the past year or so, our cleanroom facility has adopted a new technique (for us) for measuring accurate thin film thicknesses and determining thin film optical constants. To determine thin film thicknesses previously we used a profilometer which is a physical method. The method is limited in the resolution that can be obtained with several variations of probe tips, but is noisy and not always accurate particularly at very thin film thicknesses. In order to develop a better approach for measuring film thicknesses such as for coatings spun onto glass plates in the cleanroom for LCD production, an ellipsometer was brought in-house. Using this ellipsometer we are able to very accurately determine thin film thicknesses and in being able to do so, develop much better process control over our spun-on barrier layer coatings, spun-on polyimide coatings, and other coatings put down by evaporation, sputtering and e-beam methods.

Our ellipsometer is made by J. A. Woollam. It is pictured below. The model is VASE which stands for Variable Angle Spectroscopic Ellipsometer with wide spectral range of up to 193-2500nm.
J. A. Woollam Co., Inc. is a manufacturer of spectroscopic ellipsometers for non-destructive thin film and bulk material characterization. J. A. Woollam has a complete ellipsometry tutorial on their web site to explain the technique and their equipment:  http://www.jawoollam.com/ J. A. Woollam offer ellipsometers covering a spectral range to meet any need (from the vacuum UV to the far IR).

Spectroscopic ellipsometry (SE) has become the standard for measuring thin film thickness and optical constants (n and k). Spectroscopic ellipsometry is used for characterization of all types of materials: dielectrics, semiconductors, metals, organics, and more.

Ellipsometry measures a change in polarization as light reflects or transmits from a material structure. The polarization-change is represented as an amplitude ratio, Ψ, and a phase difference, Δ. The measured response is dependent on optical properties and thickness of each material. Thus, ellipsometry is primarily used to determine film thickness and optical constants. However, it is also applied to the characterization of composition, crystallinity, roughness, doping concentration, and other material properties associated with a change in optical response.

Interest in ellipsometry has grown steadily since the 1960s as it provided the sensitivity necessary to measure nanometer-scale layers used in microelectronics. Today, the range of applications has spread to the basic research in physical sciences, semiconductor, data storage, flat panel display, communication, biosensor, and optical coating industries. This widespread use is due to increased dependence on thin films in many areas and the flexibility of ellipsometry to measure most material types: dielectrics, semiconductors, metals, superconductors, organics, biological coatings, and composites of materials.

Ellipsometry is a common optical technique for measuring thin films and bulk materials. It relies on the polarization changes due to reflection or transmission from a material structure to deduce material properties, like film thickness and optical constants. This technique continues to develop as the requirement for thin film characterization increases.

For more information, check out the link to the Woollam site tutorial on ellipsometry and the links at the end of the tutorial for further reading.

Rev 1: 11/14/2007

LCI News

Prof. Wei’s Nanobioscience Lab Constructed at LCI
CPIP Professor Qi-Huo Wei’s Nanobioscience lab is now constructed and is located in room 232 of the LCI (Liquid Crystal and Materials Sciences Building. An Oxford RIE system is being installed which will allow us to fabricate micro/nanofluidic devices for biomolecule manipulation and detection.

Selinger selected as member of national board of the General Science Praxis Examination
CPIP Professor Robin Selinger reported that she has been selected as a member of the national board of the General Science Praxis Examination for teachers. She will serve for a two year term.

New Faces at LCI
Sabrina Relaix is a new postdoctoral fellow who is working in CPIP Professor Peter Palffy-Muhoray’s lab. She is from CEMES/CNRS (Toulouse, France). Her thesis title is: “Optical and electro-optical properties of capacitive cells of chiral liquid crystals”.

Woojeong Kang and Hye Young Ryu are both Samsung engineers who will be visiting for one year.
Rui Bao from HuaZhong University of Science and Technology will be working with CPIP Professor Deng-ke Yang, Sept. 07 – Aug. 08.

Student Lab Presentations are scheduled for Monday, December 3 at 4:00, and Wednesday, December 5 at 4:30.

Fall 2007 Seminars
Oct. 10: Lorenzo Marrucci, The National Institute for Nuclear Physics, Naples
Title: "Spinning" and "twisting" a light beam and other wavefront-shaping tricks performed by suitably patterned liquid crystals
Oct. 31: Ting Zhu, Department of Mechanical Engineering, Georgia Institute of Technology
Title: Modeling Hyperelastic Crystals
Nov. 7: Randall D. Kamien, Department of Physics, Univ. Pennsylvania
Title: On the Stability of Large Angle Grain Boundaries
Nov. 14: Richard J. Spontak, Department of Chemical and Biomolecular Engineering, North Carolina State University
Title: Molecular Design of Nanostructured Block Copolymers as a Route to High-Performance Electroelastomers
Dec. 5: Rafael Verduzco, Oak Ridge National Lab
Title: Self-assembled Liquid Crystal Gels
Dec. 12: L. Jay Guo, Univ. Michigan
Title: Nanoinprint technology and its application in polymer based photonic devices

Monday Liquid Crystal Research Seminars
A note about our Monday LC Research Seminars:
Liquid Crystal Research Seminars at the Liquid Crystal Institute were established as a means for local and international faculty, senior research fellows, postdoctoral fellows, alumni, visitors, industrial partners and students to share and discuss their research with colleagues.

Monday, November 5th, 2007
4:00 pm
LCI Samsung Auditorium

HIGH DENSITY CAPACITORS BASED ON COMPLEX FLUIDS AND COMPOSITES
Dr. A.B. Golovin and Prof. L.C. Chien
Liquid Crystal Institute and Chemical Physics
We discovered a new approach to design a high density capacitors based on complex fluid. The complex fluid comprises of an emulsion of water-soluble lyotropic chromonic liquid crystal, low dielectric host material, and surfactant. The formulated complex fluids enable a substantial increase in the dielectric permittivity, dielectric relaxation frequency, and relative capacitance. The complex fluid capacitors are polarity independent devices and capable of a tuned dielectric relaxation. The described design is relevant to the electrical and biological applications.

SCALING LAWS IN NANOSYSTEMS
Dr. Qi-Huo Wei
Asst. Professor Chemical Physics, Liquid Crystal Institute
Scaling laws play significant roles from macroscopic to nanometer scales in nature. For example, scaling laws dictate that small animals like insects have to be cool-blooded; scaling laws enable small animals like ants to raise items much heavier than their own weight; scaling laws allow water spiders to walk and run on the water surfaces.
This talk focuses on the scaling laws in two special nano-systems. Scaling down material sizes has led to not only unique physical properties but exciting potential applications as well for semiconductor nanowires. One example is nanowires biosensors based on field effect transistors. I will show how the scaling laws of such nanosensors can be modeled with random resistor networks and I will discuss our numerical results and ongoing experimental studies.

Another example is related to surface plasmons excited in metallic nanoparticles. I will show how the surface plasmons between nanoparticles are coupled, and how the resonant wavelength shift scales universally with interparticle distances. Especially, I will talk about how such a universal scaling law can be utilized for measuring molecular sizes in ongoing projects.

Recent Publications of LCI Director Oleg D. Lavrentovich:

Recent Conference Talks:

A note from LCI Director Oleg D. Lavrentovich (regarding the passing of Dr. Arora)
With a great sadness, I inform you that Dr. Sardari Arora, 78, passed away on November 3, 2007. In words of Dr. J.W (Bill) Doane, “Dr. Arora was the LCI's first chemist and synthesized the very first liquid crystal material for my research.”

Dr. Arora moved to Kent in 1964 as the postdoctoral fellow and then he joined the LCI as a research associate. He contributed greatly to the research that led to the first liquid crystal devices. He taught at a number of regional campuses of Kent State and retired in 1995.

Dr. Arora will be remembered as one of the founders of the liquid crystal science and the LCI.


Please let us know if you would like more detailed information about any activities at the LCI.
Phil Bos
pbos@lci.kent.edu
330-672-2511