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LOW TEMPERATURE MATERIALS GROWTH AND PROCESSING DEVELOPMENT FOR FLAT PANEL DISPLAY TECHNOLOGY APPLICATIONS

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Subj: RETURNED GRANTEE/CONTRACTOR TECHNICAL REPORTS

1. This confirms our conversations of 27 Feb 97 and 11 Jul 97. Enclosed are a number of technical reports which were returned to our agency for lack of clear distribution availability statement. This confirms that all reports are unclassified and are "APPROVED FOR PUBLIC RELEASE" with no restrictions.

2. Please contact me if you require additional information. My e-mail is *silverr@onr.navy.mil* and my phone is (206) 625-3196.

ROBERT J. SILVERMAN

FIELD EMITTER FLAT PANEL RESULTS

Anthony E. Bell, Associate Professor

Haibing Liu, Graduate Student

Objectives: To obtain uniform emission of electrons from carbon nanotube emission sites and to do so at low turn-on voltages.

Method of Approach: Grow carbon nanotubes, using different catalyst particle growth conditions; insert them in vacuum emission viewing apparatus to ascertain uniformity of emission and turn-on voltage; determine I/V characteristics.

Results: A thin catalyst film of nickel (0.4 nm thick) on a silicon substrate was reduced in hydrogen at 875 C for 30 minutes. Carbon nanotubes were subsequently grown at 950-1,000 C in less than 5 minutes. A more uniform electron emission was obtained in the vacuum testing station, compared to previous nanotube preparation techniques. Also the Fowler-Nordheim plots were more reproducible.

Work for the next quarter: We will use a TEM to inspect and characterize the size distribution of the catalyst particles in the nickel film. We will examine ways to obtain nanotubes that have open ends. Open ended nanotubes should produce much lower turn-on voltages since the effective radii of the tubes should be a few angstroms in diameter compared to up to a thousand angstroms for catalyst-particle ended nanotubes. In the current method of preparation, the catalyst particle remains at the end of the growing nanotube.

CHARACTERIZATION AND SIMULATION OF THIN FILM TRANSISTORS FOR TRANSIENT THERMAL PROCESSING

V. S. Rao Gudimetla, Assistant Professor

BACKGROUND:

The project goal is to make DC, AC, transient measurements on the TFTs, fabricated by Professor Sigmon and his group at Arizona State University using low temperature processing techniques. From these measurements, SPICE parameters will be extracted and these results will be used for process monitoring and device and process optimization for display applications. This work was started by Rao Gudimetla on 10/1/94 and this technical report is for the period 2/15/95 to 5/14/95. Some success has been reported in the fabrication of TFTs. Experimental DC I-V data was received about a month ago. We are trying to use a SILVACO simulator to compare the experimental data with simulation data to explain process reliability and device models.

RESULTS:

During the current project period, the emphasis has been to simulate some of the TFT structures fabricated by Professor Sigmon's group. Here are some key results:

1. Simulated DC I-V data is being compared with experimental data for some of the fabricated TFTs. We have started modifying the trap models and mobility models to match the experimental data against data gathered from simulation. Since the Silvaco simulator started running only recently, we have not arrived at any summary conclusions as yet.
2. We have completed the analysis of Tektronics TFTs and believe a reliable method to extract the mobility is established. We will present and publish these results. An earlier theory of the AC performance of TFTs is modified to account of rate linear region.

IMMEDIATE FUTURE PLANS:

Rao Gudimetla is on leave of absence at NASA Marshall Space Flight Center, participating in a NASA/ASEE Summer Faculty Fellowship. He is in touch actively with Professor Berglund (at OGI) and Sigmon (at ASU) and also with the graduate student, Loc Thai (at OGI) with regard to the progress of the project.

We plan to complete the following tasks in the next quarter:

1. Complete Silvaco simulation of all the TFTs fabricated with experimental data and identify the reasons for the discrepancies in this data by varying the trap and mobility models.
2. Use the above information to optimize the device processing and check our predictions on the device/processing correlations.
3. Prepare a full paper on the analysis, thus far achieved, on Tektronix TFTs.
4. Availability of experimental data will help us to investigate the electrical properties of the grain boundary for use in developing a reliable SPICE model for TFTs. We will emphasize this research aspect during the next quarter.

Electroluminescence Display Group

PIs: R. Solanki and R. Engelmann

Graduate Research Assistant: J. Ferguson

Although the amber light emitting ZnS:Mn EL phosphor has been the mainstay for several years, efficient rare-earth doped alkaline earth sulfides have been employed to produce light over a wide range of the visible spectrum, including realization of full-color displays. In this report, we shall describe achievement of violet (404 nm) light emission from SrS:Eu EL devices. This, we believe, is the first time bright visible light at such a short wavelength has been reported from EL devices. Weaker emission was also obtained at 367 nm from similar devices with Ce activator.

The Eu doped SrS EL devices were fabricated in the conventional double insulating sandwich configuration, as has been decribed in previous reports. On top of the precoated ITO/ATO glass substrates, first a 0.1 um layer of undoped ZnS was grown, followed by 0.8 um SrS:Eu, another 0.1 um ZnS, and a top insulator layer of 0.24 um Al_2O_3. A second set of devices were made without the ZnS buffer layers, i.e., SrS:Eu, followed by Al_2O_3, both of same thicknesses. All these devices were made using atomic layer epitaxy(ALE), as described previously.

The growth temperature of SrS was 375 C whereas ZnS and Al_2O_3 were grown at 425 C and 400 C, respectively. All these layers were grown following one pumpdown. After the ALE growth of the stacks, Al dots (3 mm in diameter) were evaporated on the top insulator (Al_2O_3) to serve as the back electrode.

The EL devices were powered by bipolar pulses of 30 us duration with 5 us rise and fall times, and a frequency of 1 kHz. The photoluminescent (PL) excitation source was either an Ar ion laser which was operated in the UV (~360 nm) or a mercury lamp (254 nm). The EL emission spectrum of a typical Eu doped device with ZnS buffer layers is shown in Fig. 1. The emission was bright (9 cd/m^2 at 40V above threshold,1kHz) and violet in color with a peak at about 404 nm and full width half maximum (FWHM) of 20 nm, measured with a 0.25m Jarrel-Ash spectrometer. This is a relatively bright source considering the location of this wavelength on the photoptic sensitivity curve. The CIE (Commission Internationale de l'Eclairage) chromaticity coordinates were x =0.17 and y=0.01. The corresponding PL spectrum (excited at ~360 nm) also showed a bright violet emission as shown in Fig. 1.

These results were perplexing since other research groups have reported only orange-red light from similar SrS:Eu device structures. It is likely that our ALE grown samples were unintentionally codoped with Cl, since $ZnCl_2$ was used as a precursor for the ZnS buffer layer growth. Grazing incidence x-ray analysis indeed showed, besides SrS (cubic phase) and ZnS (hexagonal phase), the presence of cubic $SrCl_2$. We should note that when SrS:Eu has been codoped with F or Cl, the result has been either a wavelength shift or a change in the emission spectrum profile of the orange red EL emission, however violet emission has not been reported.

We believe that the source of the violet emission is the parity allowed $4f^6 5d$ to $4f^7$ transition of Eu^{2+} in the $SrCl_2$ host, i.e., $SrCl_2:Eu^{2+}$. One of the earliest detailed reports of strong violet (centered at about 406 nm) photoluminescence from Eu doped $SrCl_2$ crystals dates back to 1948 [1]. More recently, several investigations have shown that Eu^{2+}in alkaline earth fluoride and chloride hosts exhibits efficient 5d to 4f emission [2,3]. In the $SrCl_2$ host the rare-earth ion occupies the metal site and is surrounded by the halides in eightfold coordination [4]. The light emission occurs at the leading edge of the driving pulse, implying electron impact as the likely excitation mechanism (Fig. 2b). It is interesting to note that recent activity in the 5d to 4f transition of Eu^{2+} doped alkaline earth halides was enticed by the possibility of achieving tunable ultraviolet and blue-green laser emission [5,6].

As the doping concentration was lowered in other devices, both the violet and the orange-red emissions were observed. It is interesting to note that after operating the dual emission devices (unencapsulated) for an extended period of time, the orange-red (SrS:Eu) emission degraded and became dimmer whereas the violet emission remained stable over several hours of operation. However, at this time we have not done lifetime studies to determine the long term stability of these devices.

Devices made without the ZnS buffer layers produced orange-red emission. The orange-red spectrum is similar to what has been reported in literature. Maximum brightness of 470 cd/m^2 (at 9 kHz) was recorded. Most of the emission occured at the trailing edge of the voltage pulse (Fig. 2c), indicating recombination as the dominant excitation mechanism, i.e., electron ionized from Eu ion to the SrS conduction band is trapped back to the $4f^6\ 5d^1$ excited state of Eu^{2+}. The de-excitation of electrons from this state to $4f^7(^8S_{7/2})$ level produces the orange light [7]. A small violet peak was also observed which was probably due to the $SrCl_2$ host formed at the SrS/Al_2O_3 interface where $AlCl_3$ was the source used to grow Al_2O_3.

A set of ZnS/SrS:Ce/ZnS devices were similarly fabricated and characterized for emission. In these structures SrS was doped with Ce only near the ZnS interfaces. EL emission was observed at about 367 nm, with a shoulder at about 344 nm (Fig. 3). This light seems to originate from $SrCl_2:Ce^{3+}$ layers and the peaks correspond to transitions from lower excited 5d states of Ce^{3+} to $^2F_{5/2}$ (344 nm) and $^2F_{7/2}$ (367 nm) states [8]. We should note that similar UV emission at 311 nm has been reported from ZnF_2:Gd EL devices [9]. The emitter in this case was identified as trivalent Gd ion. To determine the excitation mechanism of our UV SrCl:Ce devices, time resolved emission characteristics were examined. From this results we concluded that electron impact is the dominant excitation mechanism. The intensity of this emission is much weaker than the violet light. Moreover, the short wavelength of this radiation precludes it as a direct source for display applications. However, it may be possible to use the UV radiation with fluorescent dyes to produce visible light.

In summary, we have demonstrated for the first time bright violet emission from an EL device. The source of this radiation is attributed to the 5d to 4f transition of the Eu^{2+} activator in the $SrCl_2$ host formed at the SrS/ZnS interfaces. A weaker emission from $SrCl_2:Ce^{3+}$ is also reported. Although many of the alkaline earth halides are known to be moisture sensitive, they could fill the existing void due to the lack of bright blue EL sources, provided an effective means of encapsulating these layers can be found. More work is in progress to increase the brightness of the violet emission by to directly growing $SrCl_2$ EL devices.

The ALE reactor used to grow the violet emitting EL devices was recently modified to allow deposition of more uniform films from THD based Sr and Ca precursors. The quartz manifold/substrate holder has been replaced with a glass manifold and a separate reaction zone where the substrates reside. Tests are in progress to charaterize the modified reactor before quantum well phosphors are attempted. Results of these tests will be presented in the next progress report.

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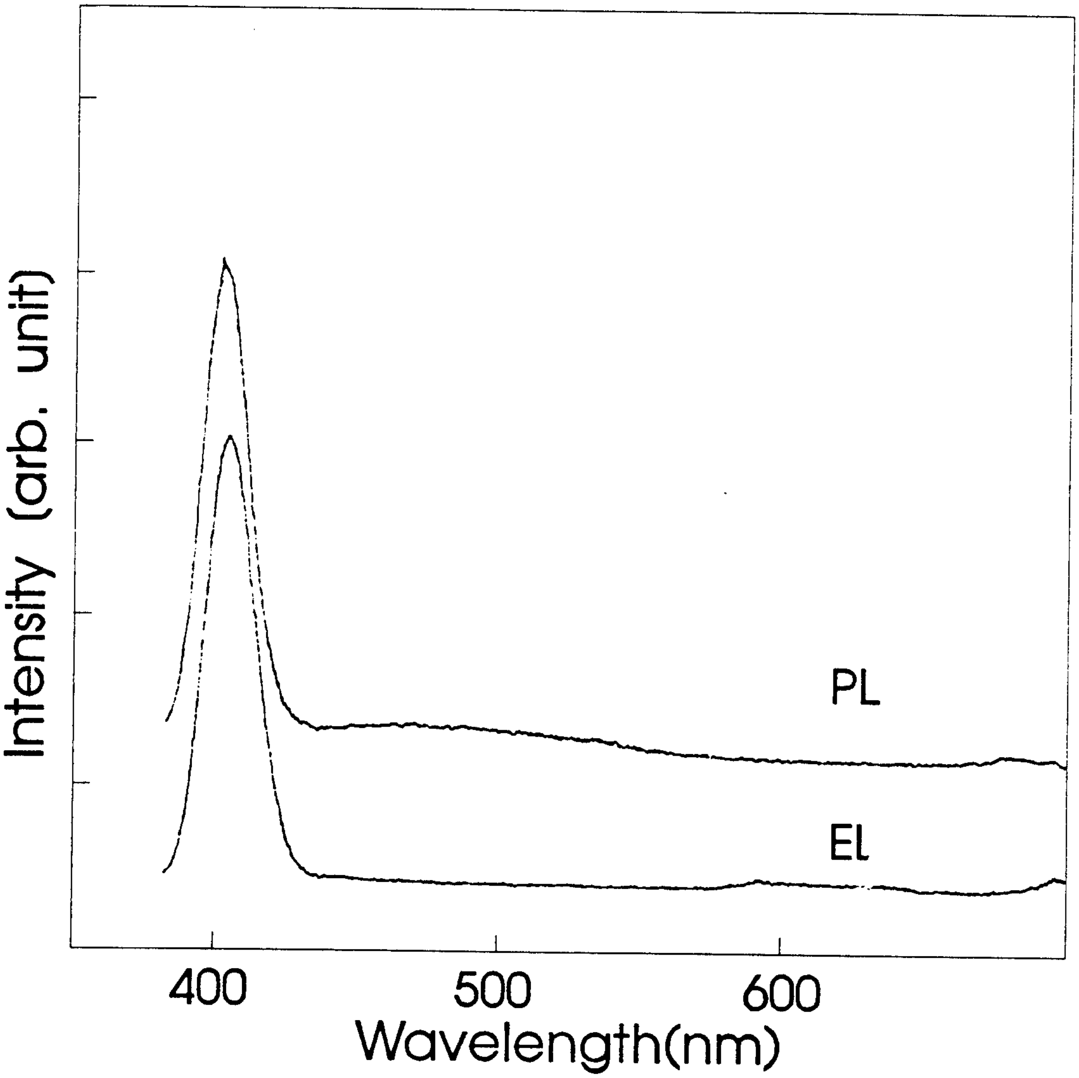
Figure Captions

Fig.1. (a) EL and PL emission spectra of the violet light emitting $SrCl_2$:Eu and (b) orange-red emitting SrS:Eu devices.

Fig.2. The driving voltage pulse (Fig.2a) and the correponding emission of violet light from ZnS containing devices (2b), and orange-red light from SrS:Eu devices without ZnS (Fig.2c) as a function of time.

Fig.3. UV EL emission from Ce^{3+} activator in $SrCl_2$ host.



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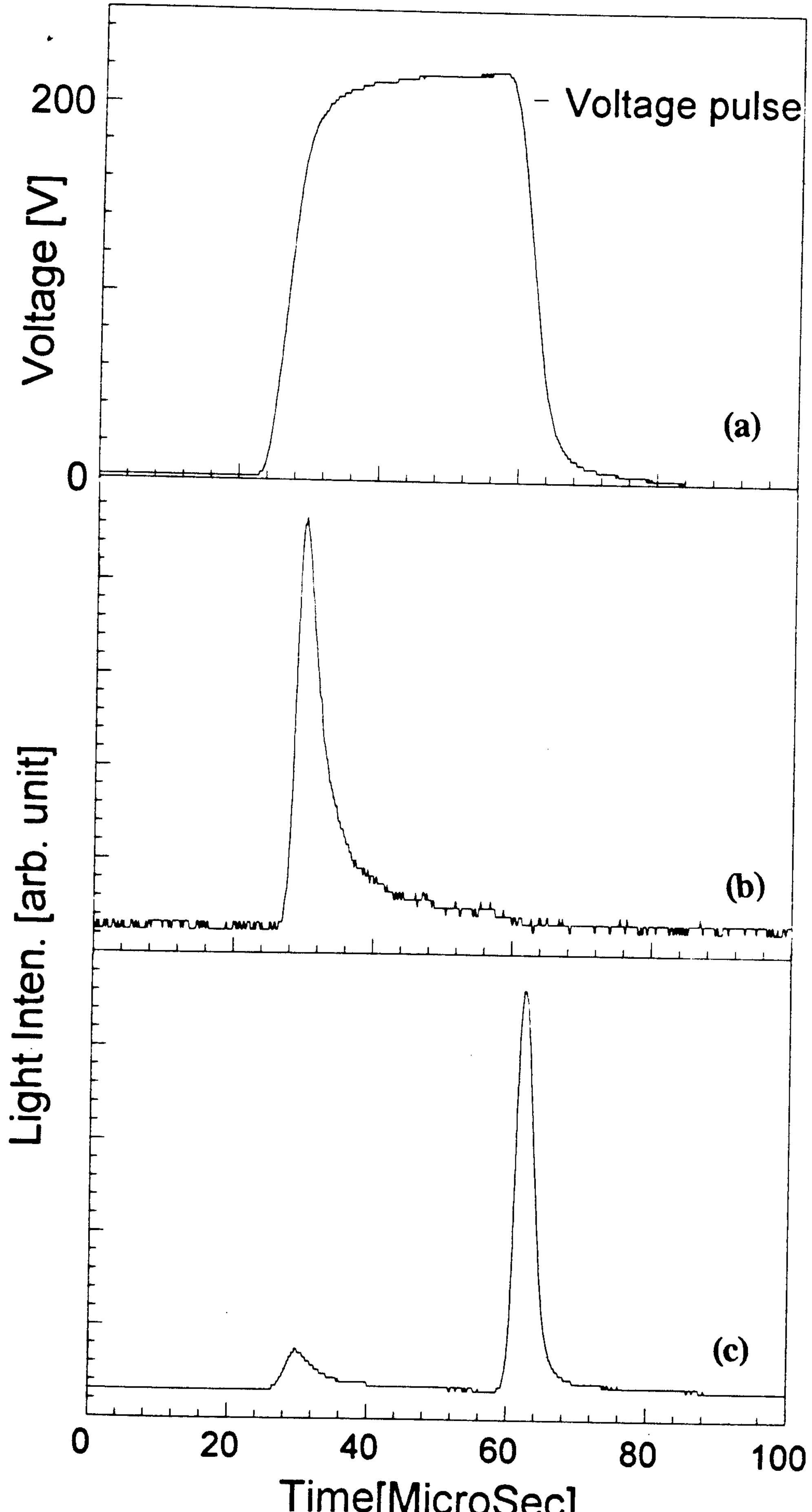
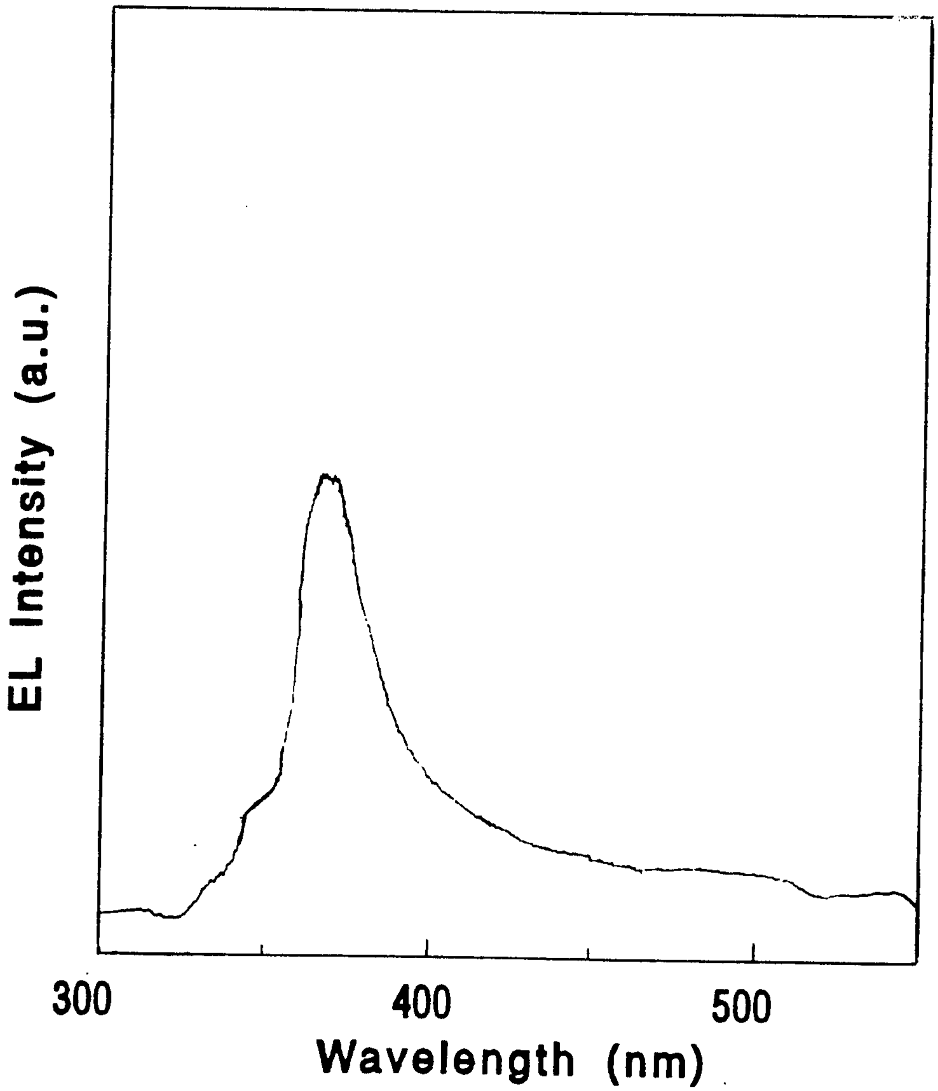


Fig.2. The driving voltage pulse (Fig.2a) and the correponding emission of violet light from ZnS containing devices (2b), and orange-red light from SrS:Eu devices without ZnS (Fig.2c) as a function of time.



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