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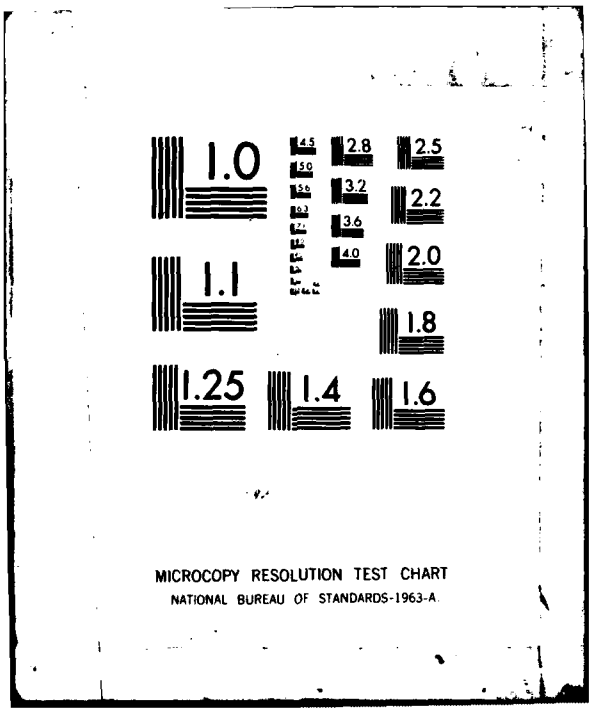
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THIN FILM LAYERED ELECTROLUMINESCENCE

FINAL REPORT

FERD WILLIAMS AND MICHAEL MARTENS

MARCH 1, 1982

U. S. ARMY RESEARCH OFFICE

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electroluminescence, collision cross-section, quantum optics, impact excitation, optical interference, phosphors

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Techniques for the fabrication of EL structures using thin film sputtering techniques, new materials to be used as efficient EL emitters, and theoretical methods by which the potential candidates for EL phosphors could be evaluated have been developed. The regions for carrier generation and collision excitation have been clearly separated experimentally and direct measurements of the cross-section for the excitation were made in systems in which the transition metal Mn is the emitting center. Measured cross-sections were

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found to be consistent with those estimated theoretically by us using a polarizability mechanism for the collision excitation process. The cross-section for Mn in ZnF_2, both measured and predicted, is 3×10^{-16} cm^2. For ZnS:Mn the cross-section is predicted to be smaller, 2×10^{-16} cm^2.

A wide variety of new materials has been investigated, amongst these the traditional cathode ray phosphors. Quantum optical effects have been studied and used to determine optical constants in thin film devices using these materials.

I. Introduction

Recent advances in thin film technology and microelectronics have resulted in the possibility of competitive electroluminescent (EL) display devices. Many of the materials considered as standard EL phosphors are well characterized in so far as their optical properties, band structure, etc., but the mechanism of light generation by applied electric field is not understood at the most fundamental, microscopic level.

The work done under this grant has sought to 1) determine the detailed physics of this method of light generation, 2) develop new materials and techniques to evaluate their efficacy, and 3) to predict, based upon bulk material properties, the specific materials that will work most efficiently in thin film EL devices. The main goal has been to separate the generation of hot electrons and the collision excitation of luminescence with contiguous semi-insulating and phosphor films.

Section II describes experimental and Section III theoretical work done during the tenure of this grant.

II. Experimental Research

A. Thin Film Electroluminescence from ZnF_2:Mn

The original goals of this effort were to develop another matrix for the Mn ion, specifically ZnF_2, because earlier work had indicated that photoluminescent films of ZnF_2 could be evaporated and would luminescence efficiently without heat treatment. ZnF_2 as a material has two characteristics which make it a more desirable matrix than others presently in use. It has a lower refractive index (larger critical angle) and should thus allow a greater percentage of the emitted radiation to pass through the film without being internally trapped. This material also needs no heat treatment, as needed in ZnS devices for phosphor restructuring and increased light emission.

Our first results confirmed the possibility of making ZnF_2:Mn thin films which electroluminesce. In the fabrication of the device which we formulated, SiO was used replacing the layer of Y_2O_3 in the standard metal-insulator-phosphor device developed by Mito. This material was chosen because it could be evaporated, as we had no facilities for RF sputtering of films at that time.

Devices could be fabricated with or without charge storage as evidenced by the hysteresis in the brightness-voltage characteristics. Analysis of the behavior of non-hysteretic devices led us to the conclusion that a fortunate thing had happened. Because the SiO is a semi-insulating material and the ZnF_2:Mn is quite conducting, essentially all of the voltage drop in the device appears across the SiO. This also means that the SiO is the source of the charge carriers which then diffuse or are field injected into the phosphor layer. These electrons continue to move within the ZnF_2, losing energy slowly to the phonons until they experience an inelastic

collision with an Mn ion. This ion, after it is excited, emits the observed 2 eV photon as it returns to the ground state.

The collision excitation mechanism is now widely believed to be the dominant one, at least for the isoelectronic centers such as Mn in various matrices. We have calculated the collision cross-section, as reported in Section III, for this process and obtain a result consistent with the experimental results measured by us for ZnF_2:Mn and by others for ZnS:Mn. These results are very encouraging and when coupled with DC EL measurements recently reported seem to give a good indication that the system inefficiency arises from the low "temperature" of the exciting electrons, 1800 K. This would imply that only a small part of the electron distribution has sufficient kinetic energy to excite the Mn. With the achievement of separation of carrier generation and light emission a program was begun to exploit this separation both as a tool to probe the fundamental processes occurring in EL devices and for its potential use in EL structures.

With the fabrication of devices in which the carriers are created in one layer and the light is generated in another it is possible to measure directly carrier mean free paths for collision excitation. Using an SiO layer as the generating layer and varying both the concentration and thickness of the ZnF_2:Mn layer, the collision cross-section for the Mn was determined to be 3×10^{-16} cm^2 in excellent agreement with that estimated theoretically and discussed in Section III. This technique is now being used to measure collision cross-sections in other phosphors.

A wide range of materials can be used in the phosphor layer. A program was begun to study a wide variety of well-known low voltage cathode ray (CR) phosphors in this type of device.

B. Device Fabrication and New Materials

We have increased our materials preparation facilities to the point at which we are now able to use RF sputtering to deposit materials. When an insulating layer of sputtered SiO_2 is used in the ZnF_2:Mn device a higher threshold voltage results because of its higher resistivity. Better stability of the films is also observed.

We now have available for sample preparation two systems. The first is that on which most samples have been made to date and consists of three evaporation stages for the semi-insulating, phosphor and metallizing layers. The second system has been designed with flexibility in mind and consists of two RF sputtering sources and two evaporation stages. The sputter guns are so oriented that simultaneous sputtering of two sources can be done without moving the substrates. In addition the metallization and/or other evaporations can be done without breaking vacuum.

With the present facilities and the separation of the carrier generating and accelerating regions as mentioned in Section I.A.,the device consists of an electron emitter and phosphor. There is no longer the same set of constraints acting on the system. To this end, new materials have been used in this device. The large set of traditional phosphors, as well as other materials, are being investigated. To date encouraging results have been obtained using ZnS:Ag, CaF_2:Mn, Zn_2SiO_4:Mn and $Ca_2Si_2O_5$:Pb,Mn. All show efficient electroluminescence when used with SiO as the electron generator. As well, all show strong quantum optical effects as discussed in the next section.

Scanning Auger profiling performed for us by Tektronix, Inc. indicates that in the SiO-ZnF_2:Mn device one has well characterized material interfaces between the layers. Use of the proton X-ray microprobe facility

available to us at the Bartol Research Foundation at the University of Delaware indicates that the ZnF_2:MnF_2 mixed powder source materials are Mn rich when compared to the evaporated layer. This is consistent with the melting points of the two materials. As well, this technique has been used as an analytical method of determining the stoichiometry of the sputtered layers. Much of the progress made in bringing the sputtering system on line has been made because this technique was available to us. Extensive modifications had to be made to the sources to guarantee that the sputter guns themselves were not contributing material to the thin sputtered films. At this time the sputtering system is on its way to becoming our primary source of new materials.

C. Quantum Optical Effects

Because of the thin film structure used in these devices, physical and quantum optical effects dominate the apparent overall device efficiency. With a correct choice of layer thickness and materials one can change the apparent color and the brightness of the device.

Using the angular dependence of the emission arising from the interference effects we are able to determine either layer thickness or index of refraction for all the constituents.

One reason for the need to correctly account for the optical interference in the devices is that this allows one to determine the real overall efficiency as a function of device and material parameters. For instance, measurements of the carrier mean free path for collision excitation have been done by observing the dependence of cell brightness at constant applied electric field for various doping levels and thicknesses of the phosphor layer. The overall apparent brightness depends on thickness. This brightness consists of both effects arising from the optical interface and effects arising from the bulk material. The two of these must be separately determined in order to determine those effects arising solely from the presence of the luminescing center.

When the measurements have been corrected for the optical interference effects, one can determine the cross-section for collision excitation by plotting the corrected brightness versus thickness. If the concentration of the luminescing center is varied at constant thickness, the effects are constant within the series of measurements and the plots can be made of brightness versus number of centers. The two sets of data can be directly compared if one uses only data in which concentration quenching effects do not appear. The combination of results derived by varying both phosphor thickness and concentration allows one to determine the collision cross-section for excitation directly.

III. Theoretical Program

Cross-section for Collision Excitation

We have recently reported on a method for computing cross-sections for impact excitation of manganese and other transition metals in ZnS and ZnF_2. The model used for this calculation assumes that the region of interest for the excitation process is well below the plasmon frequency and in the region of direct band-to-band excitations. This region of low energies is not one that can be handled by the usual high energy scattering formalisms. As an approximation of the physics of the collision process we have assumed that the incoming electron deforms the Mn^{2+} ion through a polarization of the ion. The polarization energy depends upon the proximity of the electron to the Mn^{2+} ion. The ground and excited states having different polarizabilities, a transition between the ground and first excited state of the ion will occur when the diabatic curves, those describing the potential energy of the ion-electron system, cross. The energies of the ion are calculated using a Hartee-Fock program obtained from C. Froese Fischer. We have found that the method gives good agreement with an experimental determination of the cross-section presented by Morton and Williams recently for ZnF_2:Mn. For this material the experimental and theoretical cross-sections are found to be 3×10^{-16} cm^2; for ZnS:Mn the cross-section is estimated to be 2×10^{-16} cm^2.

Included in these estimates are material properties derived from photoelectric emission data. For this method the difference between ground and excited state energies of the emitting ion and the work function and electron affinities of the crystal are used. Thus one can evaluate the cross-section for excitation knowing these parameters. The agreement with experimentally determined cross-sections is surprisingly good considering the crudeness of the approximations.

IV. Achievements and Conclusions

The main thrust during this period was to develop 1) techniques for the fabrication of EL structures using thin film sputtering techniques, 2) new materials to be used as efficient EL emitters, and 3) theoretical methods by which the potential candidates for EL phosphors could be evaluated. With the clear separation of the regions for carrier generation and collision excitation, direct measurements of the cross-section for the excitation were made in those systems in which the transition metal Mn is the emitting center. The measured cross-sections were found to be consistent with those estimated theoretically by us using a polarizability mechanism for the collision excitation process. The cross-section for Mn in ZnF_2, both measured and predicted, is 3×10^{-16} cm^2. For ZnS:Mn the cross-section is predicted to be smaller, 2×10^{-16} cm^2.

A wide variety of new materials is now being investigated.

The general conclusion on the work of this grant is that both experimental and theoretical studies can be used to direct a research program for the development of thin film EL as a viable technology. The progress that has been made in the understanding of this phenomenon is very encouraging and has injected a new enthusiasm into this field. We hope to continue to expand our understanding of this phenomenon through subsequent programs.

Appendix I

Publications Completed Under Grant

1. "A New Thin Film Electroluminescent Material - ZnF_2:Mn" by D. C. Morton and F. E. Williams, Appl. Phys. Lett. 35, 671 (1979).

2. "Some Recent Advances in Thin Film Electroluminescence" by F. Williams and D. Morton, Condensed Matter Physics (Proc. Sol. State Div. EPS) Plenum Press (New York) 1, 429 (1981).

3. "A New Multilayer Thin Film Electroluminescent Display" by D. C. Morton and F. Williams, Society for Information Display Digest 12, 30 (1981).*

4. "An Electroluminescent Display Based on Spatial Separation of Hot Electron Generation and Luminescent Excitation in Multilayer Films" by D. C. Morton and F. Williams, Proc. SID Conference 1981, New York (in press).

5. "High Field Electroluminescence" by F. Williams, J. Lum. 23, 1 (1981).**

6. "Collision Excitation Cross-Sections and Energy Levels of Deep and Very Deep Centers in Electroluminescence" by J. E. Bernard, M. F. Martens and F. Williams, J. Lum. 24/25, 893 (1981).

7. "Mechanism of Thin Film Electroluminescence" by F. Williams, M. Martens, J. Bernard, D. Morton and S. Sarwate (submitted 1982 Int. Display Conf.).

* presented at 1981 SID International Symposium; to receive Best-Paper Award at 1982 International Seminar.

** part of Proceedings of Workshop on the Physics of Electroluminescence, J. Luminescence 23, nos. 1,2 (1981) edited by F. Williams.

Patents Being Issued Under This Grant

06/142,843 (UD 8-18) Electroluminescent Structure to D. C. Morton and F. Williams.

Appendix II

Degrees Granted and Personnel Supported by Grant 1978-Present

Present Affiliation shown in parentheses

David C. Morton, M. S. (1980) (current graduate student)

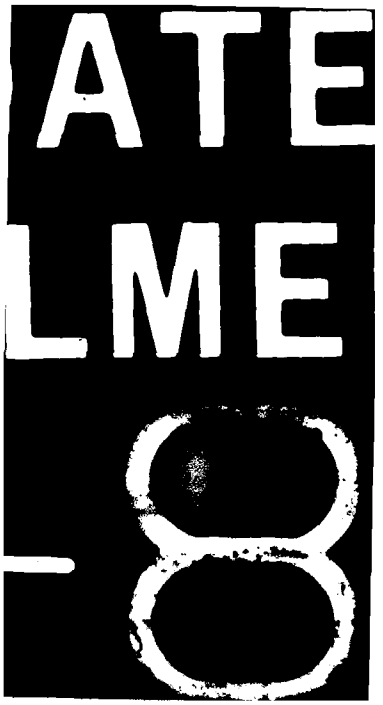
Shashank Sarwate (current graduate student)

James E. Bernard (current graduate student)

Michael F. Martens (part-time Research Associate)

David E. Berry (part-time Research Associate)

F. Williams (Principal Investigator)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