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Form Approved
OMB No. 0704-0168

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED FINAL REPORT 22 May 92 - 21 May 95
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4. TITLE AND SUBTITLE Low Temperature Epitaxial Growth of Rare Earth Doped Silicon and Silicon Germanium Alloys	5. FUNDING NUMBERS 61102F 2305/FS
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/NE 110 Duncan Avenue Suite B115 Bolling AFB DC 20332-0001	SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-92-J-0330
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11. SUPPLEMENTARY NOTES

12. DISTRIBUTION STATEMENT STATEMENT APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED	
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13. ABSTRACT (Maximum 200 words)

SEE FINAL REPORT ABSTRACT

DTIC
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JUL 28 1995

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DTIC QUALITY INSPECTED 6

14. SUBJECT TERMS	15. NUMBER OF PAGES
	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED
19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UNCLASSIFIED

JGK

~~Annual~~ ^{Final} Report to the

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

concerning the

LOW TEMPERATURE EPITAXIAL GROWTH OF RARE EARTH DOPED
SILICON AND SILICON GERMANIUM ALLOYS

Grant Numbers F49620-92-J-0330

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Original Award Starting Date: 5/20/92

EPSCoR Supplement Start: 9/1/92

Report Due Date: 12/20/94

Submission Date: 6/14/95

Accession For	
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DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
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Availability Codes	
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A. Publications

1. J. L. Rogers, W. J. Varhue and E. Adams, "Growth of Er Doped Si Films by ECR Plasma Enhanced Chemical Vapor Deposition", Rare Earth Doped Semiconductors, Ed. by P. Klein and G. Pomrenke, Mater. Res. Soc. Vol. 130, San Fransisco, (1993).
2. J. L. Rogers, W. J. Varhue, E. Adams, M. A. Lavoie and R. O. Frenette, "Growth of Er Doped Si Films by ECR Plasma Enhanced Chemical Vapor Deposition", J. of Vac. Sci. and Technol., A 12(5) 2762 Sept. (1994).
3. J. L. Rogers, P. Andry, W. J. Varhue, P. McGaughnea, Ed Adams, R. Contra, "Low temperature homoepitaxial growth of Si by ECR-PECVD", submitted to Appl. Phys. Lett.
4. J. L. Rogers, P. S. Andry, W. J. Varhue, E. Adams, M. Lavoie and P. B. Klein, "Erbium Doped Silicon Films Grown by Plasma Enhanced Chemical Vapor Deposition", submitted to Journal of Applied Physics.

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Thesis Project: Growth of Er Doped Si

Undergraduate technician: Jeffrey Seward

Introduction

This document reports on the progress towards the growth of rare earth doped Si by low temperature plasma enhanced chemical vapor deposition (PECVD). The goal of this investigation is to develop a commercially compatible technique to deposit thick, high concentration, precipitation free, rare earth doped Si films. The low temperature growth technique used is plasma enhanced chemical vapor deposition with an electron cyclotron resonance (ECR) source. Low temperature processing is needed to avoid the formation of ErSi₂ precipitates which are known to be optically inactive. Epitaxial Si films doped with varying concentrations of Er have been grown in this investigation at low substrate temperatures (<500 °C). The Er dopant sources are sublimed metal organic compounds. A total of four different metal organic compounds have been tried in the deposition process. Three of these compound were synthesized for this investigation by Prof. Kazi Ahmed

Film quality and doping concentration were determined by Rutherford backscattering spectrometry (RBS). Recently, film quality has also been analyzed by X-ray diffraction rocking curves and cross sectional transmission electron microscopy. The X-ray technique has been made available through an NSF-EPSCoR equipment grant to the University of Vermont.

If a large concentration Er or other rare earth element doped Si can be grown, the potential for electrically pumped lasers and optical amplifiers will be greatly increased. This would open up an entirely new field, silicon light emitters for Si based devices.

Research

These past months we have continued to make progress toward the the deposition of Er doped Si films with the goal of fabricating light emitting devices. Some of the research highlights will be outlined below.

1. Epitaxial film quality: The goal from the beginning was to develop a process that would deposit Er doped Si in a fashion that could be commercially viable. One major obstical to this goal was the dreadfully low deposition rates that were obtainable from our process. An additional obstical was the overall crystalline quality of the epitaxial material that was deposited. Major progress has been made in both of these fronts. The deposition rate has been increased from 30 Å/min to 60 Å/min at present. The increase in deposition rate has been obtained by changing several process parameters such

as: in-situ cleaning process, power, substrate temperature and process gas composition. The system has recently been installed with 100% silane and further deposition rate increases are expected.

The epitaxial quality has actually improved at the higher deposition rates, most likely due to the decreasing percentage of contamination from the reactor with the higher silane flows. Film quality is determined by high resolution x-ray diffraction. An example of an epitaxial film spectrum superimposed on that of a bare Si wafer is shown in Figure 1.0. The deviation observed from the bare sample is quite small and most likely due to some stress relief at the interface.

2. Incorporation of Optically Active Er complexes in Si.

Initially, the majority of Er doped samples were prepared with the metal organic compound, [Tris (2,2,6,6-tetramethyl -3,5-heptanedionato) erbium (III)]. The results from these investigations have been written up and submitted to the Journal of Applied Physics. A copy of this manuscript is included. In summary this was not a good MO source to use for this particular application. It was unstable in the deposition environment and did not efficiently lead to the incorporation of optically active Er complexes in Si.

Several samples using the Bis-(tri-methylsilyl) erbium amide, have been prepared and initial photoluminescence results indicate an order of magnitude increase over that of the previous compound, Figure 2. We have prepared several new samples under the new growth conditions discussed above and are awaiting photoluminescence characterization by Dr. Robert Hengehold of AFIT. The initial results were very promising.

3. Fabrication of light emitting structures.

An optical mask set has been designed and fabricated to to make a variety of light emitting structures. To date we have fabricated simple PN junctions mainly to test the process of co-doping the Si films during growth with Sb using a small Sb sputter target . A simple I-V curve for a diode is shown in Figure 3. This appears to be a very nice means to obtain PN structure.

One of the goals of the overall project is to fabricate a light emitting device which utilizes impact ionization to excite the optically active Er centers. As previously proposed, we intend to fabricate this device on a heteroepitaxial insulator, namely Y_2O_3 . It appears that our attempts to deposit a heteroepitaxial Y_2O_3 buffer layer have been successful as determined by x-ray diffraction. An x-ray spectrum of

the heteroepitaxial Y_2O_3 on (100) Si is shown in Figure 4. We are currently attempting to deposit an epitaxial Si film on this material.

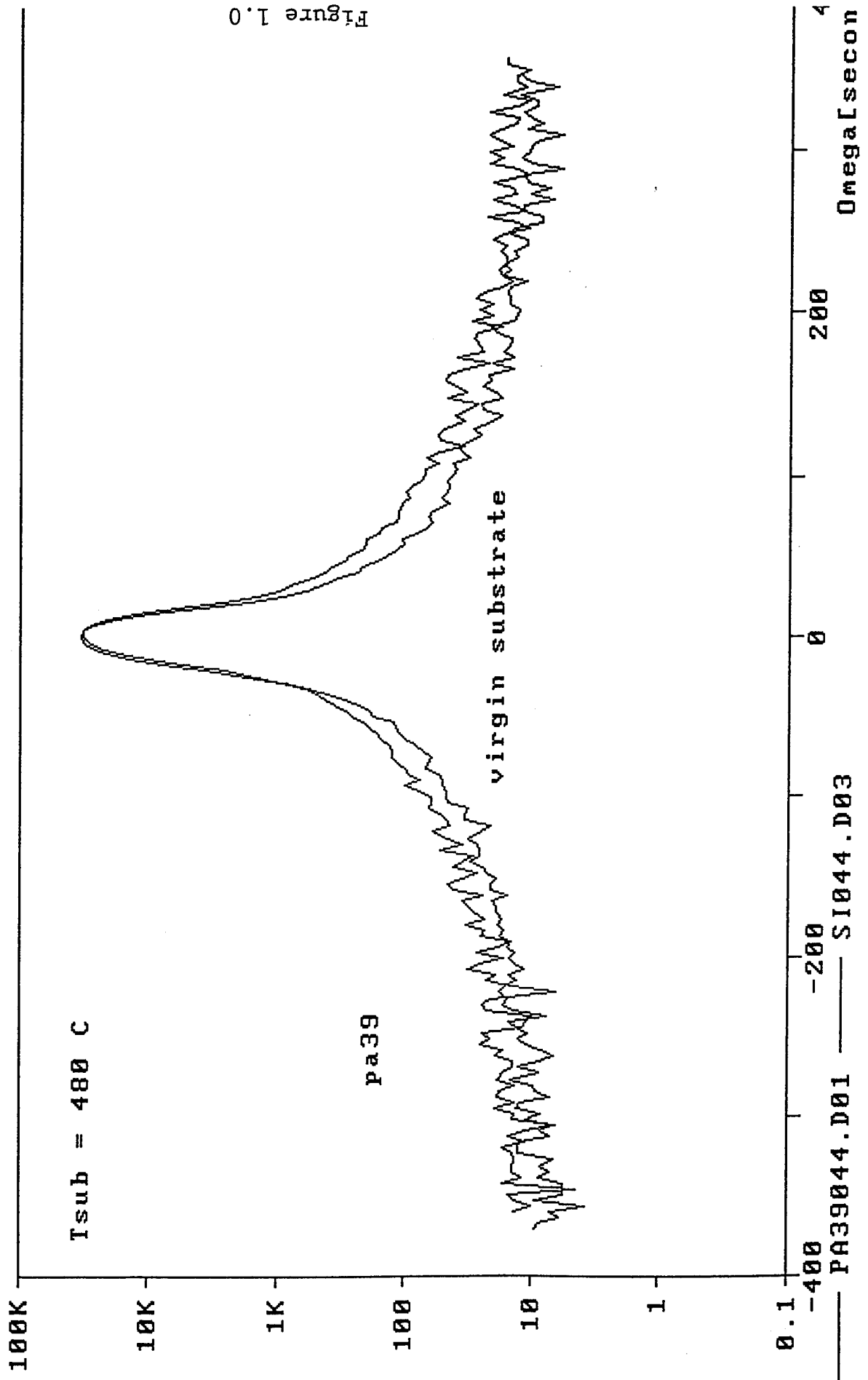


Figure 1.0

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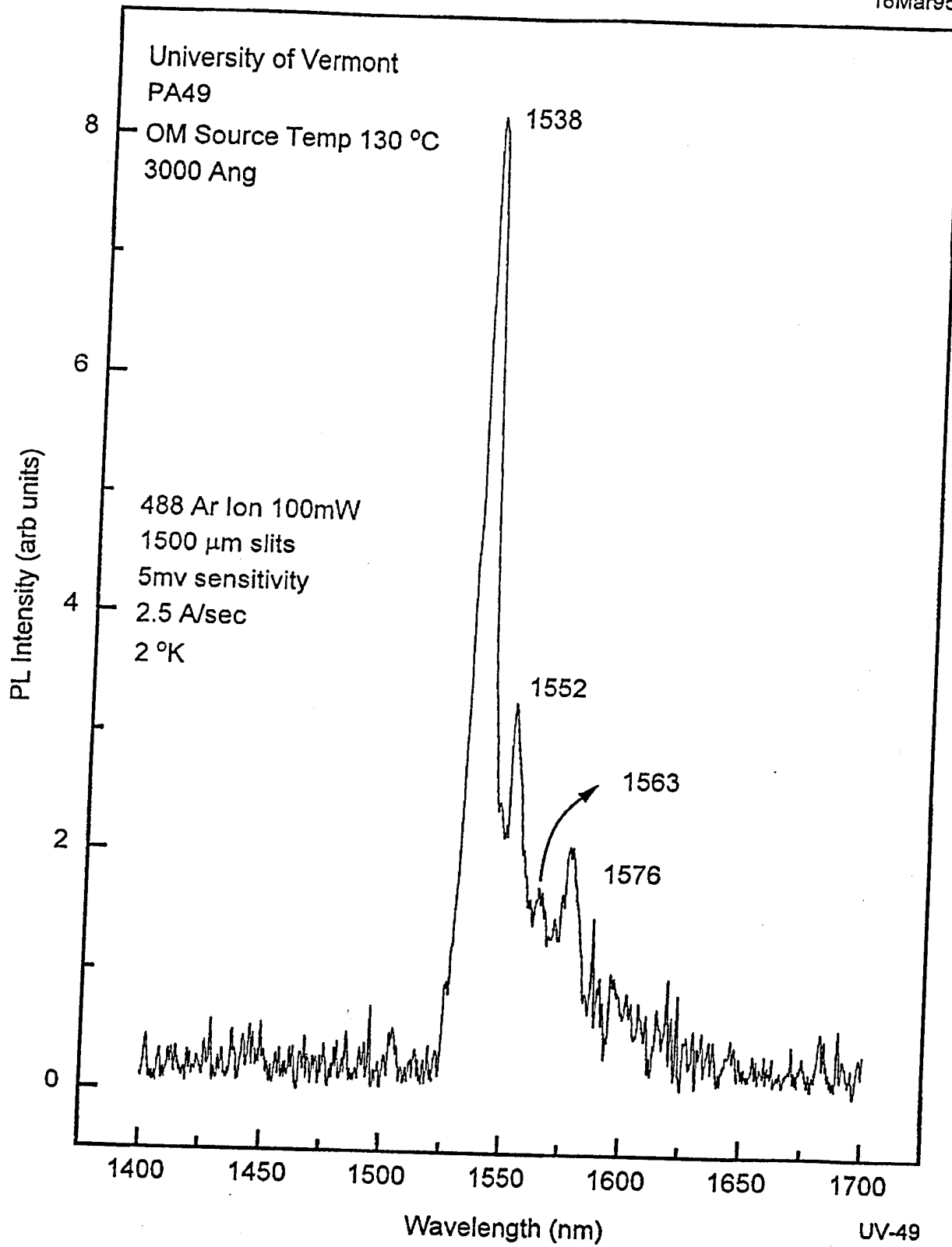


Figure 2.0

Sb-doped epi on p-type wafer (3 mm mesa)

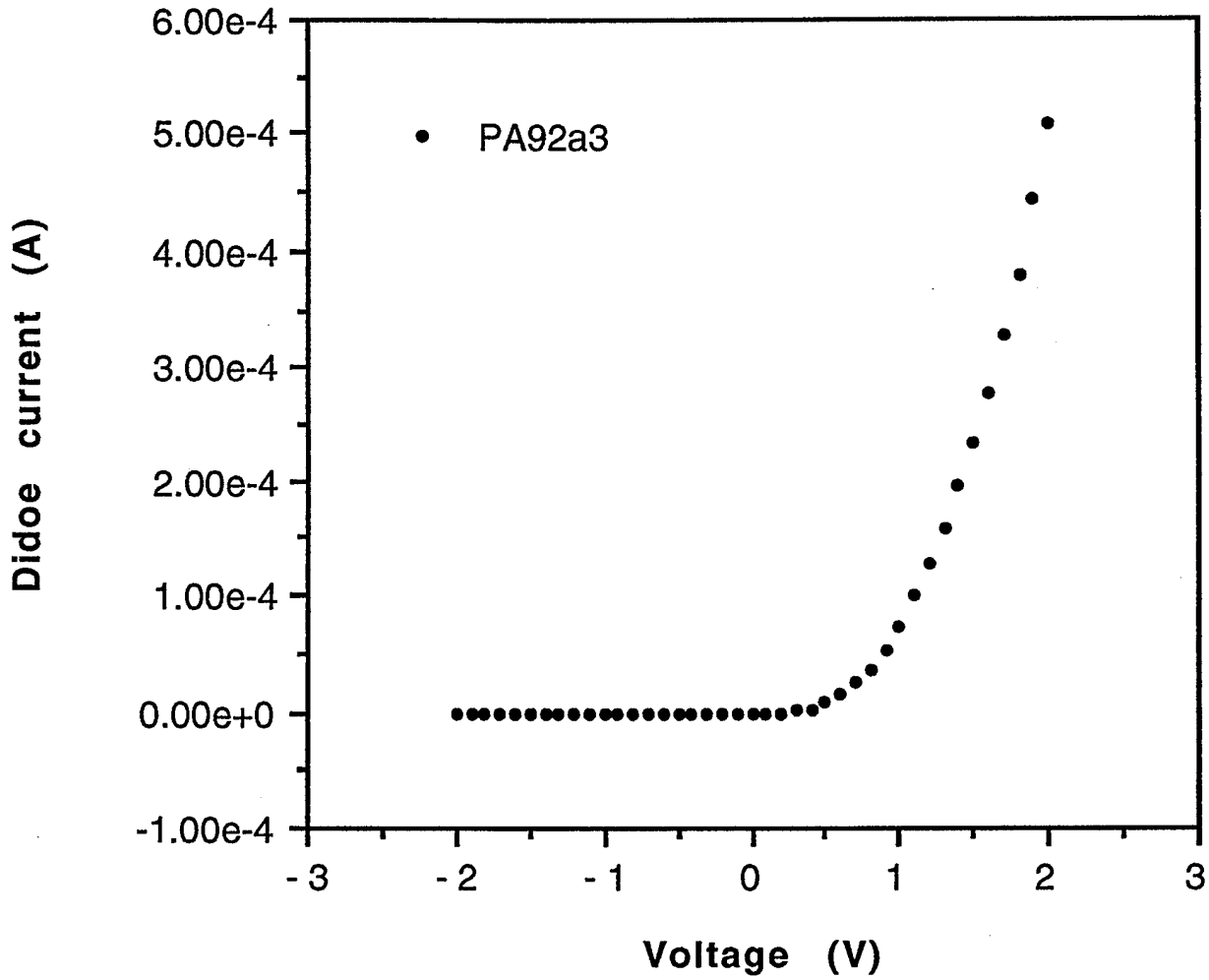


Figure 3.0

hk1 0 0 4 Omega 22.50000 Phi 275.31
4500 2Theta 45.00000 Psi 0.770

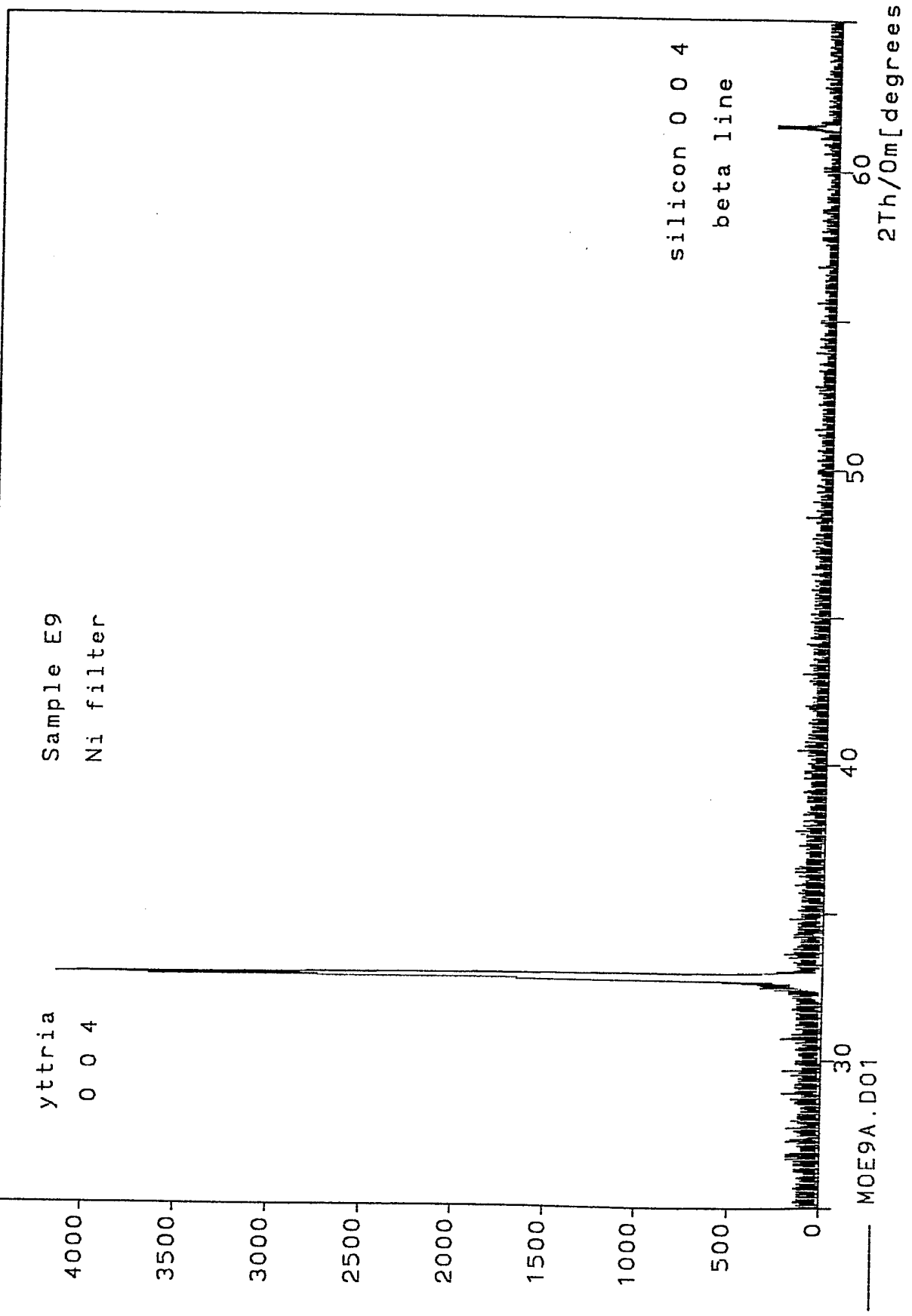


Figure 4.0

Erbium doped silicon films grown by plasma enhanced chemical vapor deposition

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Abstract

Epitaxial growth of erbium doped silicon films has been performed by plasma enhanced chemical vapor deposition using an electron cyclotron resonance source. The goal was to incorporate erbium as an optically active center, (ErO_6), through the use of metal organic dopant sources. The characteristic 1.5 micron emission was observed by photoluminescence. Chemical analysis of the film revealed however that the organic ligands were decomposing and contributing to the carbon contamination of the films. Analysis of the molecular flux to the substrate indicated that the metal organic compound used, (thd)Er, was most likely to decompose, and supply unbonded atomic erbium and not the optical active species, ErO_6 . Excessive carbon contamination lowered epitaxial quality and reduced the photoluminescent intensity. Photoluminescent intensity was improved by a 600 °C anneal but was strongly quenched by a 900 °C anneal. The low temperature anneal improved crystal quality, and the high temperature anneal resulted in silicide formation.

Introduction

As computing technology advances there is tremendous demand for increased information processing capacity and higher data transmission rates. The use of optical interconnection is one solution which offers virtually unlimited bandwidth and eliminates delay time due to finite line capacitance and resistance. Optical interconnection further provides immunity to crosstalk and electromagnetic interference. In the field of integrated circuit technology, silicon is the most widely used material due to its abundance, electrical and physical properties and its ability to grow a high quality thermal oxide. These properties have contributed to the development of a highly evolved silicon integrated circuit technology. To implement optical interconnection in Si, optoelectronic devices must be integrated with electronic circuits on the same die. Considerable interest has recently been focused on the use of rare earth dopants in Si as the route to obtain light emitting devices. This follows from the initial demonstration by Ennen et al.¹ in 1984 of light emission from Er doped Si. Erbium is of particular interest due to its sharp luminescence at 1.54 μm , which corresponds to the minimum absorption and dispersion window for silica based optical fibers.

Luminescence from rare earth elements arises from an internal transition in the 4f shell which is screened by the outer lying 5s and 5p shells. This shielding by the outer lying shells causes the luminescence wavelength and the spontaneous transition lifetime to be independent of the host material. Erbium's luminescence originates from the $^4I_{13/2}$ to $^4I_{15/2}$ transition in the $4f^{11}$ shell of the Er^{3+} ions. In the free ion case, this transition is forbidden by the parity selection rule (Laporte Rule). It is the crystal field of the host that makes the transition possible. The crystal field of the host intermixes states of opposing parity and splits the free ion energy levels into multiple sublevels². It is the magnitude of the crystal field that determines the degree of parity mixing, and it is the degree of parity mixing that controls the transition probability. Therefore, the transition probability can be changed by modifying the crystal field surrounding the Er atom.

The excitation process begins with either the production of electron-hole pairs by the absorption of sufficient energy or by free carrier injection from an adjoining structure. Electron-hole pair recombination then feeds energy into the Er ion complex via an Auger-like process³. Luminescence intensity is related to how efficiently the Er ion acts as a recombination center. The crystal field of the surrounding silicon lattice alone is small, and translates into a small interaction cross section and a long spontaneous emission lifetime for the Er center⁷. The result is a small transition probability for the $4f^{11}$ state of Er in a Si lattice. The capture cross section of Er in a silicon host could be increased if the microenvironment that surrounds the Er^{3+} atoms could be modified.

The intensity of luminescence has been shown to increase linearly with increasing Er

concentration in CZ silicon until the concentration reaches about 5×10^{17} atoms/cm³.^{4,5} By increasing the oxygen content in the samples, Priolo et al.⁶ demonstrated that this saturation in the luminescence intensity was caused by a lack of oxygen atoms. Correlation of the Er and oxygen distributions suggests the formation of Er-O complexes. Extended x-ray absorption fine-structure (EXAFS) measurements^{7,8} indicated that the nearest neighbor to Er in Czochralski grown silicon is oxygen and that this is a requirement for the Er to be an optically active center. The magnitude of the crystal field around the Er atom is a function of the orientation and chemical nature of the ligands bound to the Er ion. As a result, it is the local chemical environment around the Er ion that is the largest factor in determining its optical activity. The larger electronegativity of oxygen results in a much stronger ligand field surrounding the erbium ion in Er-O complexes compared to Er-Si complexes.

An additional factor which directly influences the density of optically active Er centers is the concentration of Er permitted in solid solution in the Si lattice. Ion implantation is by far the most widely used method to incorporate Er into a Si host lattice. Although ion implantation is a non-equilibrium process which allows the introduction of high concentrations of Er in Si, implantation results in a large amount of lattice damage which necessitates a high temperature anneal. Following the annealing cycle, the excess Er precipitates in the form of ErSi₂ which is optically inactive. In order to maintain the crystal quality and avoid ErSi₂ precipitation, a low temperature, non-thermal equilibrium process is required to deposit high quality epitaxial Si.

Finally, to realize useful optoelectronic devices using Er doped Si, efficient room temperature luminescence is required. Luminescence is observed to decrease with temperature however as a result of increased competition by other recombination processes. The higher temperature increases the activity of defects which act as fast non-radiative recombination centers and also increases the likelihood of backtransfer from the excited Er complex. It is important therefore that the Er centers be incorporated in a defect free lattice in order to achieve room temperature luminescence.

The goal therefore is to deposit high concentrations of optically active Er centers in defect free Si at low overall process temperatures. Previous attempts to increase luminescence have included molecular beam epitaxy (MBE)⁹⁻¹², metalorganic chemical vapor deposition (MOCVD)¹³⁻¹⁵, metalorganic vapor phase epitaxy (MOVPE)^{16,17}, solid phase epitaxy^{18,19}, RF sputter deposition^{20,21}, and pulsed laser irradiation^{22,23}. Conventional CVD techniques using SiH₄ would be preferable from an economic basis, however substrate temperatures as high as 900 °C are required. Very low pressure CVD, at 10⁻³ Torr, deposits epitaxial silicon films at temperatures of between 650 °C¹³ and 800 °C²⁴, but these process temperatures are too still high to avoid precipitation of ErSi₂. In a plasma-enhanced CVD process the energy from the glow discharge allows the deposition to occur under non-thermal equilibrium conditions, permitting the substrate

temperature to be lower. Epitaxial silicon films have been grown at temperatures ranging from 200 °C²⁵ to 300 °C²⁶. Due to their low deposition temperatures, plasma enhanced methods could be instrumental in obtaining high concentration, defect-free Er doped silicon thin films.

An attractive plasma enhanced process for this application is that of Electron Cyclotron Resonance (ECR) PECVD. Microwave power is resonantly coupled to electrons gyrating in a magnetic field. The newly liberated electron absorbs additional energy from the microwave field and collides with gas species to produce additional ionization and/or chemically reactive species from the process gas. This process of electron-ion production continues until about 5 % of the plasma is ionized. An ECR plasma is typically operated on the order 10⁻³ Torr, and generates ion densities of up to 10¹² cm⁻³. Through this process, ions are accelerated toward the substrate with energies of 10 eV to 20 eV in the ECR plasma stream. Low ion energies are necessary in order to avoid ion bombardment damage to the growing film (the threshold energy for atom displacements in Si is 13.0 eV).

The process of incorporating optically active Er complexes in the Si lattice without the need for additional high temperature processing will be attempted through the use of metal organic compounds. Volatile metal organic precursors containing Er in desired optically active bonding arrangement are available. The high vapor pressures of the metalorganic compounds allows their transport in gas lines to the deposition chamber by a carrier gas such as Ar or H₂.

Beach et al.¹³ used MOCVD to deposit erbium doped silicon using tris-1,1,1,5,5,5-hexafluoro-2,4-pentanedionato erbium (III). Crystalline samples with 2x10¹⁹ atoms/cm³ were grown, with the epitaxial quality being limited by the incorporation of fluorine, carbon and oxygen into the films. This contamination was due to the incomplete removal of the organic ligands, a problem that is a major obstacle to the use of metalorganics. Metalorganics, with their large organic ligands, can lead to a carbon concentration that is orders of magnitude larger than the erbium concentration. This much carbon can destroy the epitaxial growth of the film leaving useless carbon rich amorphous layers. To avoid this problem, the metalorganic and the deposition process must be optimized such that the organic ligands do not break apart after releasing the erbium atom on the film surface.

Erbium doped epitaxial silicon thin films were grown on silicon substrates using an Electron Cyclotron Resonance Plasma Chemical Vapor Deposition (ECR-PECVD) process. The metalorganic compound Tris(2,2,6,6-tetramethyl-3-5-heptanedionato)erbium(III) was chosen. This metalorganic is a pink powder with a melting point of 168-171 °C and a boiling point of 290 °C. The compound was obtained from Strem Chemicals, Inc. The chemical composition of this metalorganic is Er(C₁₁H₁₉O₂)₃ and it has an atomic weight of 717.08 (AMU). This particular metalorganic was selected for two reasons. The first reason is it has a vapor pressure of 0.1 mm Hg at 160 °C, this vapor pressure makes it possible to deliver a controlled

reactant stream with a mass flow delivery system. The second reason is that the ligands are attached to the Er ion through two oxygen atoms, six in total. All available information indicated that this compound would break apart preferentially at the C-O bonds and not the Er-O bonds. If this is true, then this metalorganic should leave an Er atom surrounded by three or six oxygen atoms in the deposited film creating an optically active center. Chemical reactivity of the metalorganic with the reactor ambient or thin film surface is also important to avoid unwanted incorporation into the Si film.

Experimental Setup

The ECR reactor used in these experiments is constructed of stainless steel and is diagramed in Figure 1. Base pressure in the reactor is maintained at 1×10^{-8} Torr levels by a turbomolecular pump that is backed by a roots blower and a rotary mechanical pump. A throttle valve is positioned between the process chamber and the turbomolecular pump, which allows process pressure to be controlled independently of total gas flow. A load-lock chamber is used to insert samples into the reactor clamped onto a silicon carbide coated graphite substrate block. Consequently the reactor is always maintained at high vacuum, even during sample transfer. Microwave power enters the reactor through a quartz window. The ECR region is located about 11 cm in front of the the microwave window and travels approximately 30 cm before reaching the substrate holder.

Once the load-lock is under vacuum, the gate valve separating the load-lock and the reactor is opened and the substrate block is transferred to the substrate holder in the reactor. There is a thermocouple on the substrate holder that slips into the substrate block in order to monitor the sample temperature.

Process gas enters the reactor at two different locations, argon enters the reactor next to the quartz window and the metalorganic and silane enter through separate gas rings about 10 cm in front of the substrate holder. All process gas used are ultra high purity grade which is 99.999 % pure. The metalorganic is placed in a stainless steel "bottle" that is located in a low temperature (200 °C maximum) oven. A mass flow controller is used to regulate the flow of Ar carrier gas through the MO Er source. Heat tapes surrounding the gas line between the bottle and the reactor keep it 10 °C warmer than the source temperature in order to prevent condensation.

Sample Preparation

All samples were 5 cm by 3 cm and were cut from (100) n-type or p-type 4 inch Si wafers. Samples were first degreased in trichloroethane at room temperature for 5 min, followed by a rinse in methanol. The samples were then rinsed in DI water and placed in a 10 % HF solution for 30 seconds to remove the native oxide. The samples were rinsed again in DI water, dried and clamped onto the substrate block. The substrate block was then placed in the load-lock chamber

evacuated and moved into the deposition chamber.

The in-situ clean consists of a Ar (50 sccm) and H₂ (20 sccm) plasma etch for 5 min at the deposition temperature. The in-situ plasma clean is used to remove native oxide that may have formed since the HF dip as well as remove any organic material still on the sample surface. The benefits of this low energy plasma clean have been demonstrated⁴⁷⁻⁴⁹. The deposition is started immediately after the plasma clean without extinguishing the plasma. This is accomplished by simultaneously stopping the H₂ flow and starting the flow of 10 % SiH₄ in Ar.

Before beginning deposition, the gas line connecting the metalorganic source to the reactor was preheated along with the substrate block. Once film deposition started, the metalorganic source was heated to a pre-determined temperature. Approximately 10 min before the deposition ended, the metalorganic source was turned off and cooled back down to room temperature by the end of the deposition. The metalorganic delivery line was maintained at temperature until the end of the deposition. This procedure was followed to prevent contamination of the line for subsequent growths.

The MO source was loaded with approximately 3 grams compound and pumped down to the vacuum level of the reactor ($\sim 10^{-8}$ Torr). Initially the oven temperature was ramped up to 120 °C, and held there for 30 min. to degas any water that may have been absorbed by the metalorganic powder. The pressure in the bottle was monitored by a capacitance manometer.

Process Diagnostics

The gas composition in the plasma chamber was monitored by a quadrupole mass spectrometer with a mass range of 0 to 300 AMU (atomic mass units). The quadrupole was located in a differentially pumped chamber separated from the main chamber. The orifice was located behind the substrate holder with a direct line of sight parallel to the axis of the ECR reactor when the substrate holder is removed.

A gridded ion energy analyzer was used to perform the ion energy and ion current density measurements at the substrate location. The energy distribution of the ions entering the analyzer is obtained by slowly raising the bias on the ion repeller and recording the current at the collector. The ion energy and ion current measurements were performed separately from the depositions.

Sample Characterization

Crystalline quality as well as the erbium concentration was determined by Rutherford Backscattering Spectroscopy (RBS). X-ray diffraction was also used to determine crystalline quality. For RBS analysis crystalline quality is determined by the ratio of the channeled backscatter intensity to the random angle backscatter intensity (X_{min}). While RBS is an excellent technique for obtaining Er content in the films, it has a low sensitivity for other lighter mass

contaminants. Therefore, Secondary Ion Mass Spectroscopy (SIMS) was used to determine the impurity concentrations of carbon, oxygen, and hydrogen in the silicon films. By monitoring the mass spectrum of the sputtered ions with time, a depth profile of the impurities can be produced. SIMS is the only surface analysis technique that is sensitive enough to detect doping level concentrations in semiconductor materials.

Photoluminescence (PL) measurements were performed at 10 K on the samples to verify the optical activity of the erbium in the crystalline films. The optical pumping source for the PL measurements comes from the 514.5 nm line of a argon ion laser used to illuminate the sample. The energy from the laser is absorbed in the top 1 μm of the silicon, causing the generation of electron-hole pairs. The electron-hole pairs travel through the film and recombine, some at erbium defect sites. Recombination at the erbium site excites the Er^{3+} ion, which then emits radiation around 1.54 μm . This spectrum from the Er^{3+} sites is detected by a liquid nitrogen cooled germanium detector.

Discussion of Results

Growth of Erbium Doped Silicon

Silicon films were grown using the following conditions: 200 to 500 W microwave power, 5 mTorr reactor pressure, argon gas feed to the resonance chamber, 10 % silane in argon gas feed to the substrate region, and a substrate temperature of 400 $^{\circ}\text{C}$. The resulting growth rate from these conditions was approximately 2.0 nm/min. The Er content of the deposited films was controlled by the temperature of the metal organic source. A plot of the resulting Er concentration in the deposited films as a function of source temperature is given in Figure 2. Increasing the MO vapor flux had a detrimental effect on the crystalline quality. A graph of the RBS X_{min} values as a function of Er concentration is shown in Figure 3. The X_{min} of the samples averaged around 10 % until an Er concentration of 2×10^{19} atoms/cm³ was reached, at which point the film quality deteriorated rapidly and eventually amorphous. The maximum amount of Er that was incorporated while still maintaining crystalline film growth, was 2.5×10^{19} atoms/cm³.

Luminescence Results

Photoluminescence measurements were performed on samples grown with different film thicknesses and levels of Er doping. The photoluminescence spectra for three representative samples is shown in Figure 4. The sample number, film thickness, Er source temperature, RBS X_{min} value and measured Er concentration are presented in Table 1. Comparing this data with the relative emission intensity it appears that intensity increases with film thickness for the same doping level and slightly with increasing Er concentration.

Other studies using ion implantation⁸, have demonstrated that a 30 min 900 $^{\circ}\text{C}$ anneal of the

sample is required after the film growth to optically activate the incorporated Er. In an effort to increase the luminescence intensity of the samples, the following anneal cycles were performed on separate pieces: a. low temperature anneal (60 min. at 600 °C in forming gas), or b. high temperature anneal (60 min at 600 °C followed by 30 min 900 °C in forming gas). The results of these annealing cycles are shown in Figure 5. For the amorphous sample, both anneal options reduced the luminescent intensity. This result is interpreted as the loss of optically active centers to silicide formation. The solid solubility of Er in silicon is 1×10^{18} atoms/cm³ at 900 °C, thus silicide production in this sample had a large driving force. For both crystalline samples, the low temperature anneal increased luminescence whereas the high temperature anneal reduced luminescence. The increased luminescence at 600 °C for the two crystalline samples is attributed to the improvement in carrier lifetime associated with improved crystalline quality and the optical activation of the Er atoms by reaction with oxygen. The reduction in luminescence at the 900 °C is probably due to a reduction in the density of optically active Er centers due to the formation of Er silicide.

Carbon and Oxygen Contamination

The deterioration in epitaxial film quality with increasing Er concentration, was investigated with the aid of SIMS analysis. This analysis technique provided carbon and oxygen concentration profiles, as well as Er and hydrogen ion count profiles. Absolute Er concentrations values were determined by RBS measurements. An undoped Si film sample was grown and analyzed to determine the typical carbon and oxygen background concentrations due to contamination in the reactor. The carbon concentration was measured to be 7×10^{18} atoms/cm³ and oxygen was 1×10^{20} atoms/cm³. The oxygen content appears to be high considering that it was grown in a ultra high vacuum chamber where the oxygen partial pressure was measured to be less than 10^{-10} Torr. These values for carbon and oxygen concentration were compared to levels measured in samples doped with Er to determine the contribution of the MO ligands.

The SIMS depth profile of Er in the films is shown in Figure 6. The uniformity of the Er concentration during film growth was independent of the film thickness and independent of the metalorganic source temperature. The sublimed MO system is delivering a constant amount of Er to the reactor during the growth period. The hydrogen concentration profile was constant through the entire thickness of the film with the exception of the interface which shows a peak resulting from the argon/hydrogen plasma pre-clean before film growth.

A plot of typical SIMS oxygen profiles is shown in Figure 7. Oxygen concentrations were also uniform throughout the film thickness with the exception of a 50 % increase at the film-substrate interface. Since deposition is initiated immediately following the pre-clean cycle, the higher oxygen level initially would appear to be due to the incomplete removal of the oxide from

the substrate surface. A graph of oxygen concentration as a function of Er concentration in the film is shown in Figure 8. Oxygen content appears to be constant and independent of the Er concentration in the film, until an Er concentration of 3.5×10^{19} is reached. The ratio of oxygen/Er atoms starts at 15 oxygen/Er atoms for an Er concentration of 7×10^{18} atoms/cm³ and decreases with increasing Er concentration until a ratio of 6 is reached at an Er concentration of 2.5×10^{19} atoms/cm³. The ratio for oxygen/Er atoms in the MO compound is six, indicating an additional source of oxygen in the process which is significant at low doping levels. Only at high doping levels does the correct ratio of oxygen/Er appear in the film.

Carbon concentration profiles were also measured using SIMS analysis, two examples are shown in Figure 9. Unlike oxygen and hydrogen, there was no increase in carbon concentration at the film-substrate interface. A plot of the carbon versus Er concentration in the films is shown in Figure 10. This plot shows a corresponding increase in carbon concentration with increasing Er concentration in a ratio of approximately 33 to 1, corresponding to the stoichiometric ratio of carbon/Er atoms of the metalorganic, $\text{Er}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3$. This indicates that the ligands of the metalorganic are breaking up, and are being incorporated into the film. For films deposited with high Er concentrations there is enough carbon to poison the epitaxial growth of the film.

A mass spectrum of the flux of chemical species impinging on the substrate surface was observed with the quadrupole mass spectrometer system described above. The purpose was to observe how the compound breaks up in the plasma. Actually, what was measured was the electron impact decomposition of the OM compound to 30 eV electrons supplied by the quadrupole's ionizer. Although these electron energies are on average higher than those experienced in the plasma, the results can give some insight into the fate of the OM compound. A background mass spectrum was first obtained with 3 sccm of argon flowing through the unheated metalorganic bottle. The source temperature was raised to 120 °C and another mass spectrum was taken. The net mass spectrum and likely mass species observed for masses greater than above 150 AMU is given in Table 2.

There were over thirty peaks of varying magnitudes in the MO mass spectrum. This discussion will be limited to the four largest peaks and the peak with the largest mass. Assuming all peaks to have the to have the same appearance potential, the largest peak occurs at mass 168 AMU, corresponding to the atomic mass of Er. The mass of one complete MO ligand attached to the Er is 183 AMU, and this is the second largest peak. The third and fourth largest peaks are 196 AMU and 184 AMU, and represent ErOC and ErO molecules respectively. Finally, the largest mass observed was 234, which is the mass of ErO_6H_2 . From this analysis, most of the MO compound appears to be breaking apart at the Er-O bonds forming elemental Er and $\text{C}_{11}\text{H}_{19}\text{O}_2$. This result is disappointing from the perspective of incorporating intact, optically active ErO_6 fragments. Further these results corroborate the problems encountered with carbon contamination

in the films. Other factors which could contribute to the incorporation of carbon into the films includes ion induced dissociation of the MO ligands, reaction of hydrogen with the ligands, and thermally activated dissociation of the ligands adsorbed on the growth surface. Energetic ions or electrons in the plasma collide with the MO molecule and cause it to dissociate, both in the gas phase or adsorbed on the film surface. However, from the above investigation with energetic electron bombardment, the complete dissociation of the MO ligand was not observed. Instead, the metalorganic tended to break preferentially at the Er-O bonds, resulting in Er atoms and intact $C_{11}H_{19}O_2$ ligands.

Atomic hydrogen in the gas phase and on the growth surface may also play a role in the dissociation of the metalorganic ligands. Hydrogen radicals are created by the dissociation of silane in the plasma and are highly reactive. These radicals could react with the carbon in the metalorganic ligands. To test this hypothesis, two samples were prepared under identical conditions with the exception of an additional 2 sccm of hydrogen added to the feed. The growth rate of the film without hydrogen was 2.4 nm/min, and this increased to 2.9 nm/min with the hydrogen addition. Composition analysis determined by SIMS measurements indicated that the carbon concentration of the sample grown with hydrogen was 70 % larger than that of the sample grown without hydrogen. This demonstrates that the hydrogen in the reactor during the deposition is contributing to the the dissociation of the metalorganic. Furthermore, the oxygen concentration of the sample grown with hydrogen was 170 % larger than the sample grown without hydrogen. This increase in oxygen content is too large to be attributed to the dissociation of the metalorganic. The only possible explanation for this large increase in the oxygen is that the hydrogen is etching the quartz window where the microwave power enters the reactor. Oxygen from this etching reaction then travels with the plasma stream to the substrate surface. The production of oxygen through the etching of the quartz window by hydrogen created in the dissociation of silane also explains the relatively high concentrations of oxygen in the silicon samples (1×10^{20} atoms/cm³), compared to the low partial pressures of oxygen ($< 1 \times 10^{-10}$ Torr) in the ultra-high vacuum level of the reactor.

Rutherford back channeling results for the sample grown without hydrogen had a X_{\min} of 6.0 % while the sample grown with hydrogen had a X_{\min} of 10 %. The extra carbon and oxygen in the sample as a result of the hydrogen in the plasma, reduced the epitaxial quality of the film by 65 %. The epitaxial quality of the film is clearly dependent on the level of contamination in the film. Reducing this contamination by preventing the etching of the quartz window is necessary to improve the general quality of epitaxial Si films grown by this process in general. The immediate solution to the problems encountered with the particular MO source used in this investigation is to find another compound which is has smaller ligands which preferentially dissociates at the ligand/oxygen bond and not the oxygen /Er bond.

Conclusions

Erbium doped epitaxial silicon films have been grown with concentrations as high as 5×10^{19} atoms/cm³ using the metalorganic compound Tris(2,2,6,6-tetramethyl-3-5-heptanedionato)erbium(III), (thd)Er. The low temperature PECVD process used to grow the films permitted the incorporation of Er into the crystal lattice at concentrations 25 times the solid solubility of Er in silicon at 900 °C.

The MO compound, (thd)Er, chosen for these experiments was expected to deposit optically active ErO₆ on the growth surface in order to maximize the luminescence intensity. Secondary Ion Mass Spectrometry measurements performed on the films demonstrated that this was not the case. Instead it was shown that all of the carbon and oxygen from the metalorganic ligands were also incorporated into the films. Energetic electron and ion bombardment, and reaction with atomic hydrogen from the dissociation of silane in the plasma contributed to the observed breakdown of the metalorganic. The carbon contamination from the metalorganic increased proportionally with the Er concentration eventually preventing epitaxial growth. The largest source of oxygen contamination was from the microwave window in the ERC reaction chamber.

It would appear that the crystal growth is not limited by the Er concentration, but instead, the carbon contamination. As a result, Er concentrations higher than 2.5×10^{19} atoms/cm³ are obtainable using this technique if a more appropriate MO is chosen. Such a MO would have to be more resistant to the harsh environment of plasma CVD, and preferably have fewer carbon atoms per ligand.

Photoluminescence measurements on epitaxial samples annealed at 600 C showed an increase in luminescent intensity due to the improvement in crystal quality and bonding for optically active Er centers. Luminescence decreased for annealing temperature of 900 C due to the formation of silicides.

Acknowledgements: The support of the Air Force Office of Scientific Research is gratefully appreciated.

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Table 1. Measurements made on selected Er doped samples

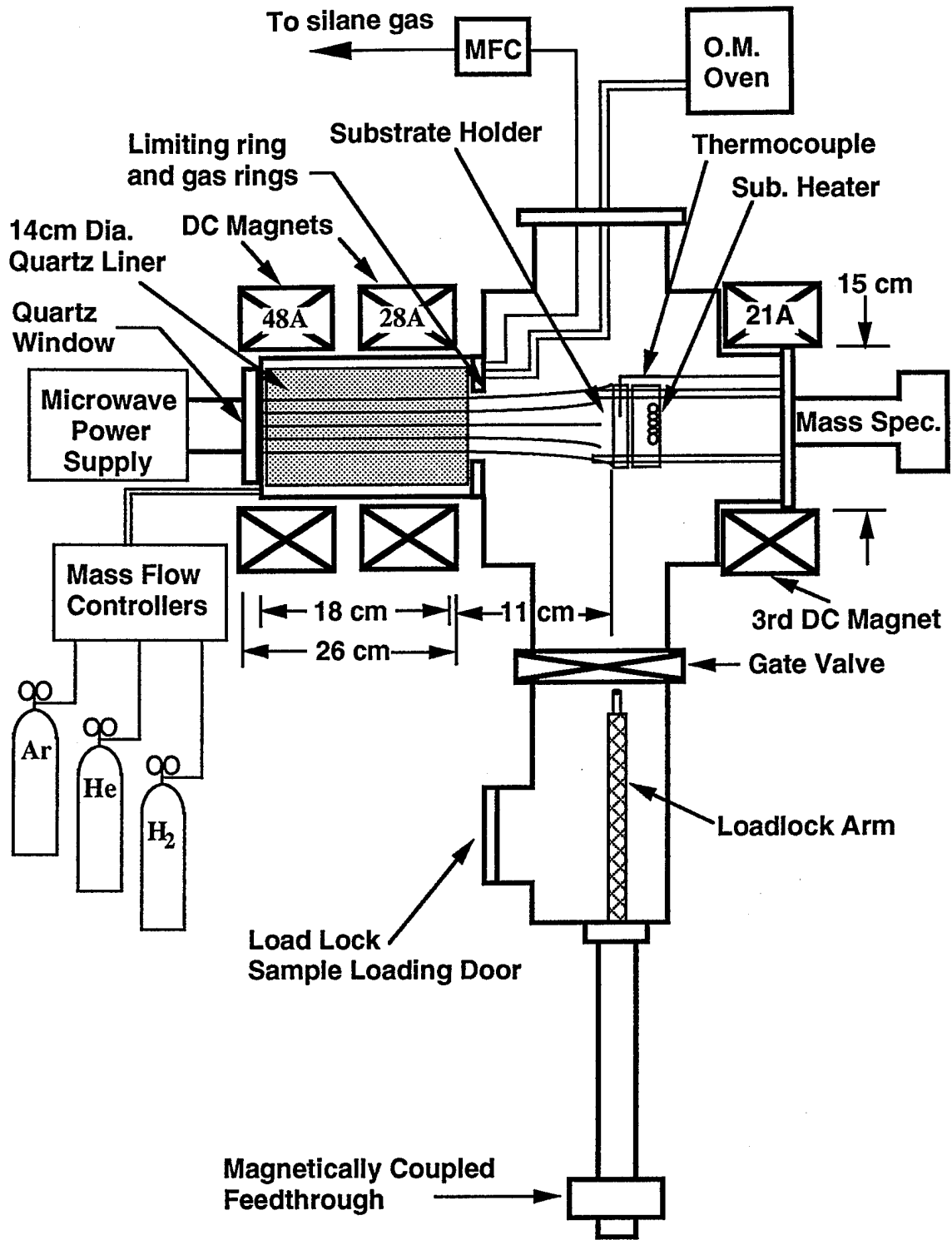
Sample	Film Thickness	Er Source Temperature	RBS X_{\min}	Er Concentration
1	1500 Å	68 °C	24 %	$7.5 \times 10^{18} \text{cm}^{-3}$
2	2800	68 °C	24 %	$7.5 \times 10^{18} \text{cm}^{-3}$
3	2800	74 °C	amorphous	$5.0 \times 10^{19} \text{cm}^{-3}$

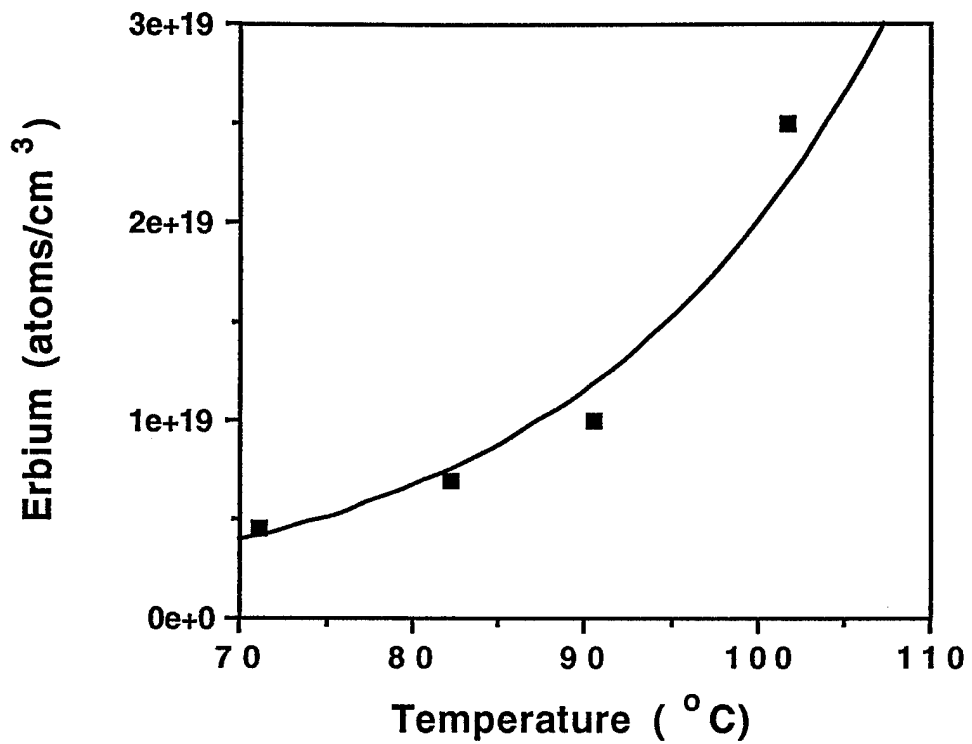
Table 2. Er metalorganic mass peaks and their corresponding spectrometer collector currents.

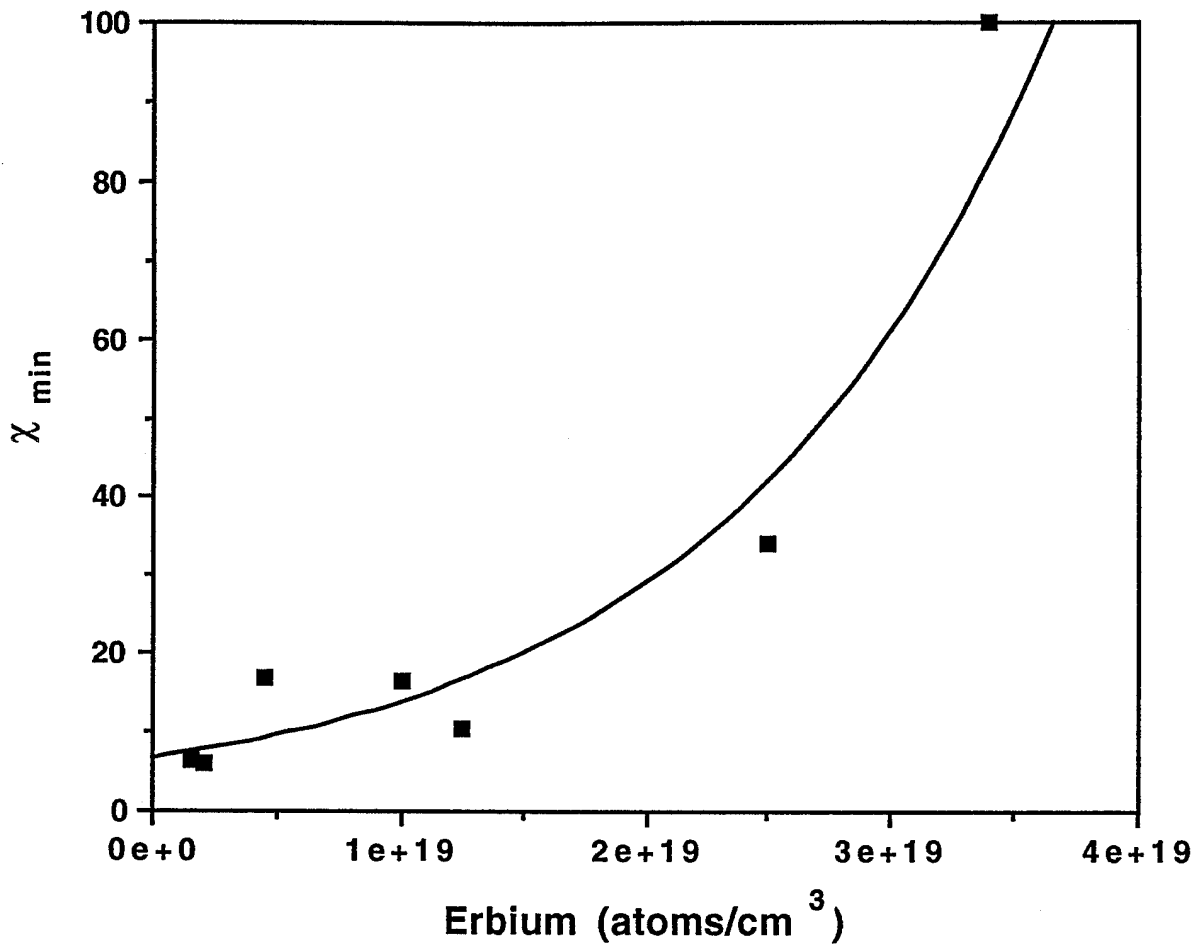
Mass (AMU)	Possible Species	Collector Current ($\times 10^{-13}$ A)
168	Er	43
183	$\text{C}_{11}\text{H}_{19}\text{O}_2$	22
184	ErO	6.1
196	ErOC	7.5
234	ErO_6H_2	0.18

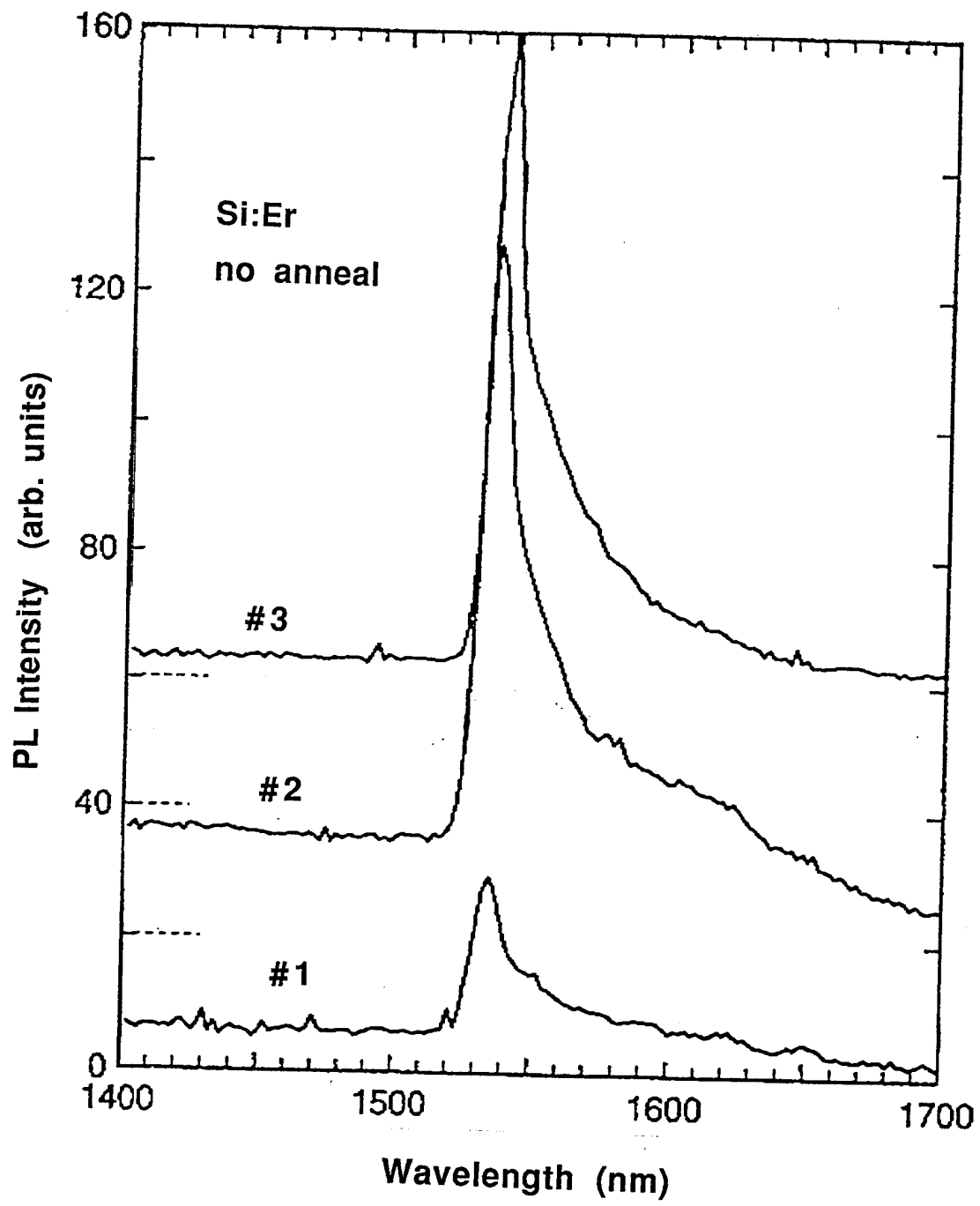
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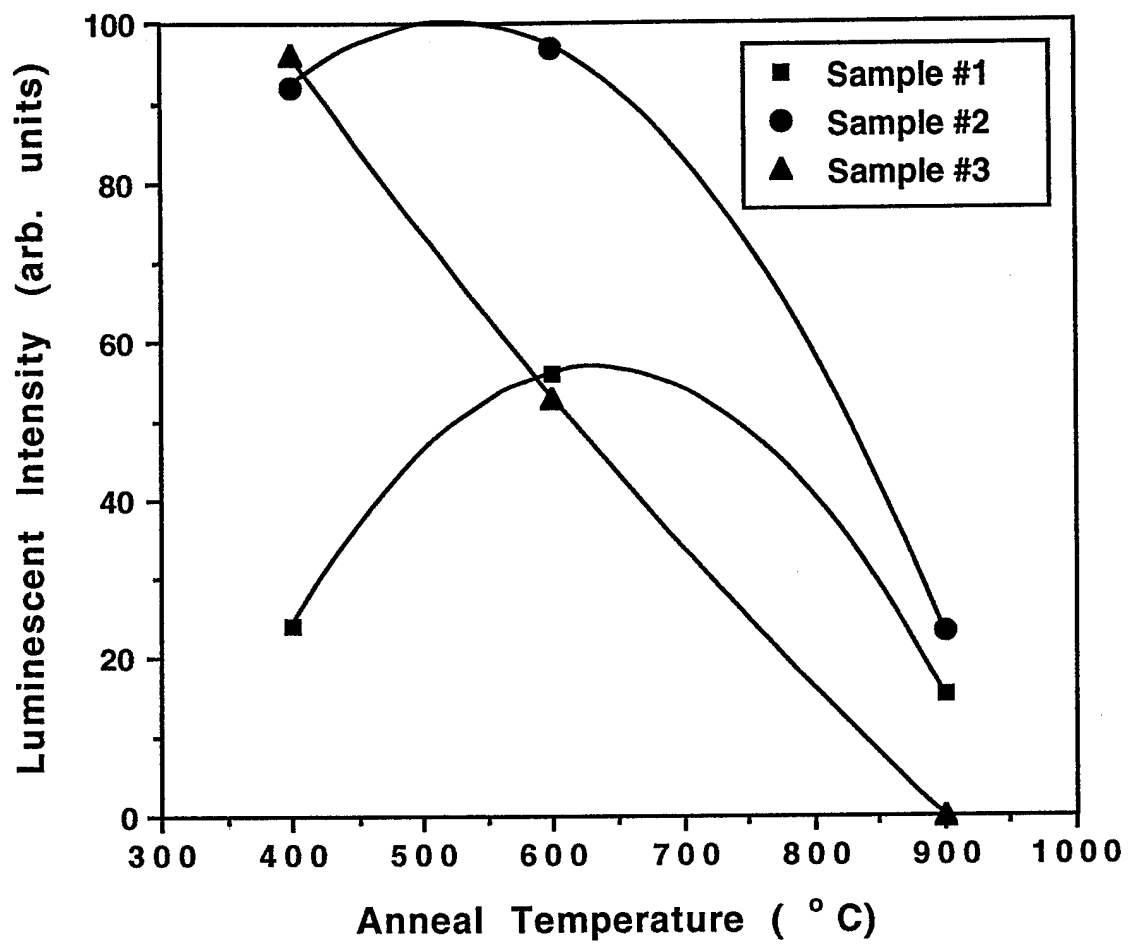
- Figure 1. Schematic diagram of the ECR-PECVD deposition system.
- Figure 2. Erbium concentration in the films as a function of metalorganic source temperature. Deposition conditions: 0.5 sccm silane, 5 mTorr, 500 W, and 400 °C.
- Figure 3. Rutherford back channeling values as a function of Er doping concentration.
- Figure 4. Photoluminescence spectra for Er doped Si samples corresponding to Er concentrations and thicknesses of: 1). $7.5 \times 10^{18} \text{cm}^{-3}$, 1500 Å, 2). $7.5 \times 10^{18} \text{cm}^{-3}$, 2800 Å, and 3). $5.0 \times 10^{19} \text{cm}^{-3}$, 2800 Å.
- Figure 5. Photoluminescence intensities at 1.54 μm emission for Si samples annealed at 600 °C and 900 °C. These are the three samples whose unannealed emission spectra are shown in Figure 4.
- Figure 6. Erbium concentration profiles determined by SIMS for two different MO source temperatures.
- Figure 7. Oxygen concentration profiles determined by SIMS for two different MO source temperatures.
- Figure 8. Oxygen concentration in the films as a function of Er concentration. Deposition conditions: 0.5 sccm silane, 5 mTorr, 500 W, and 400 °C .
- Figure 9. Carbon concentration profiles determined by SIMS for two different MO source temperatures.
- Figure 10. Carbon concentration in the films as a function of Er concentration. Deposition conditions: 0.5 sccm silane, 5 mTorr, 500 W, and 400 °C.

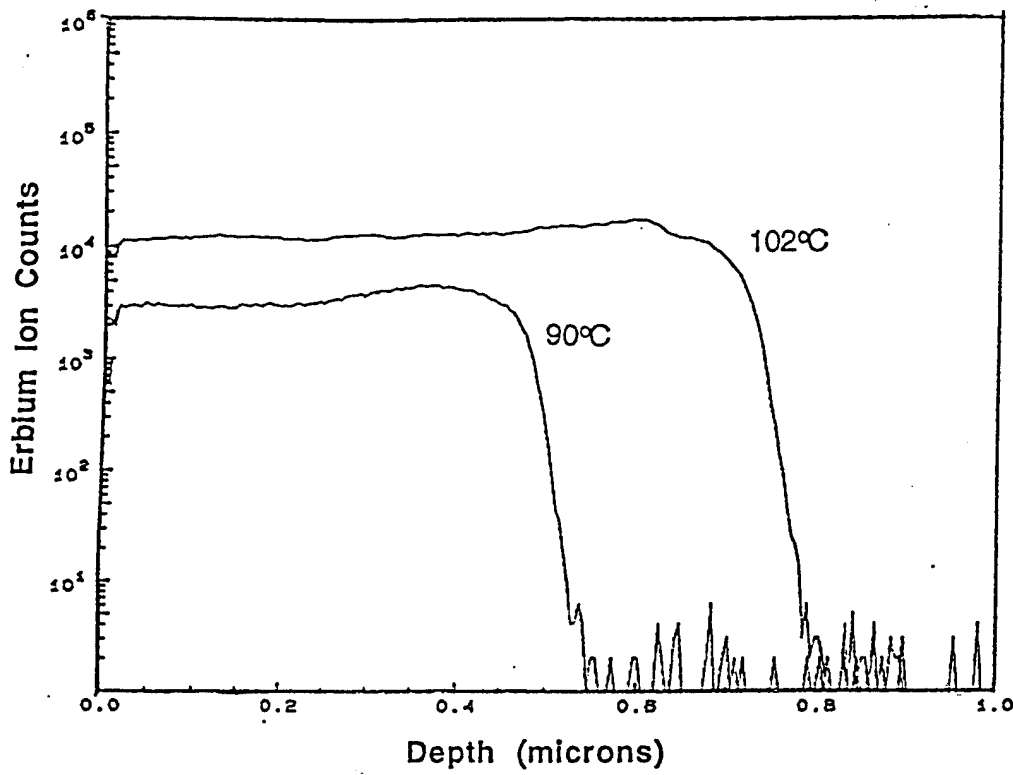


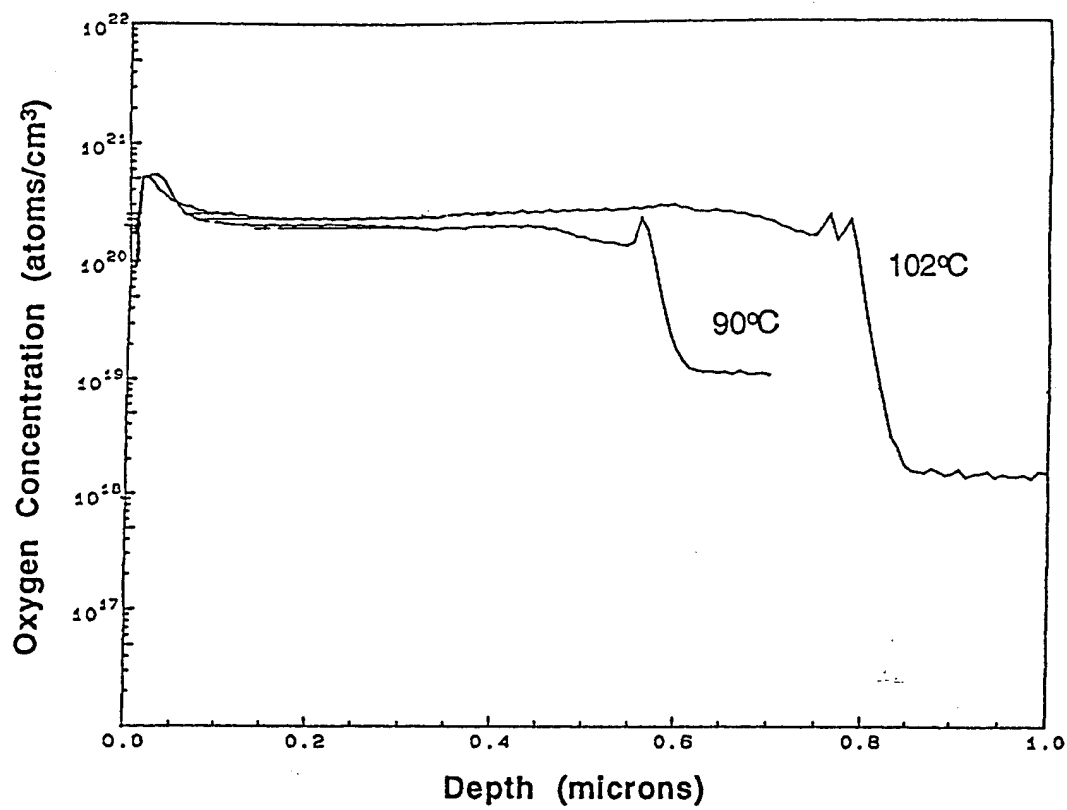




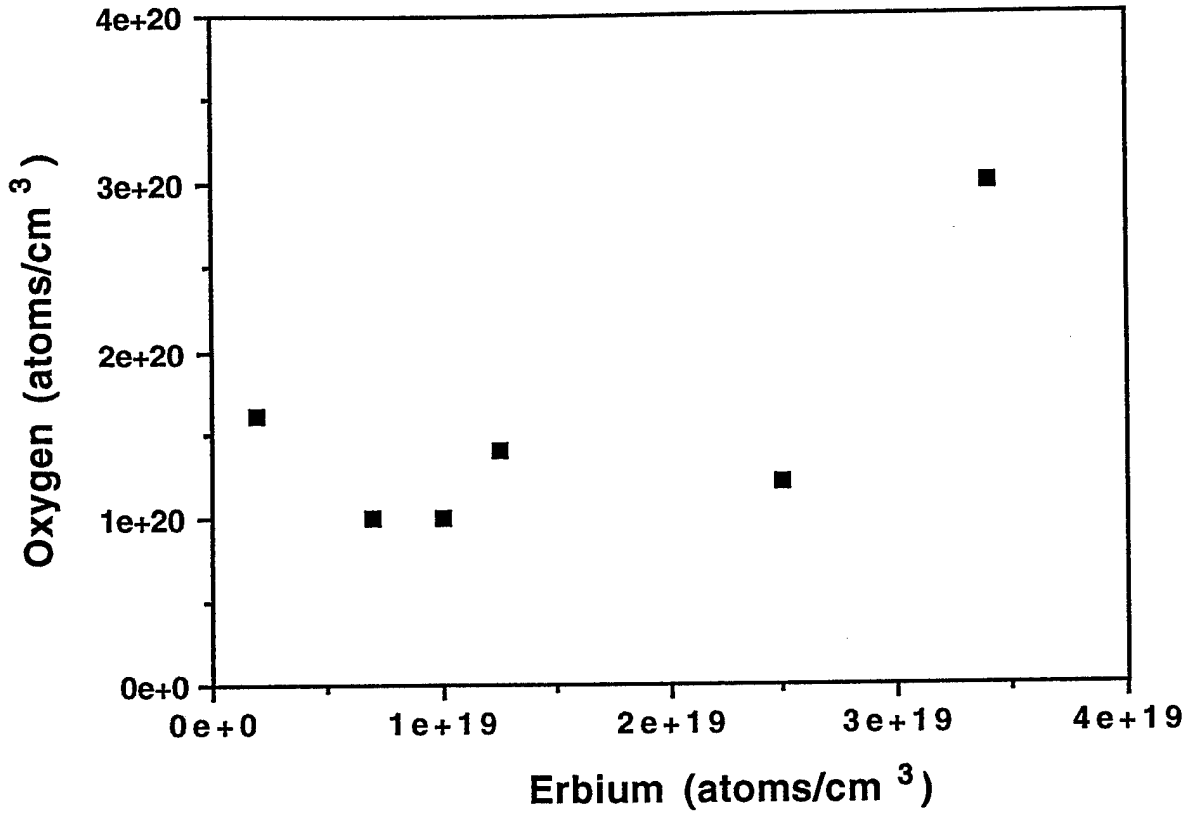


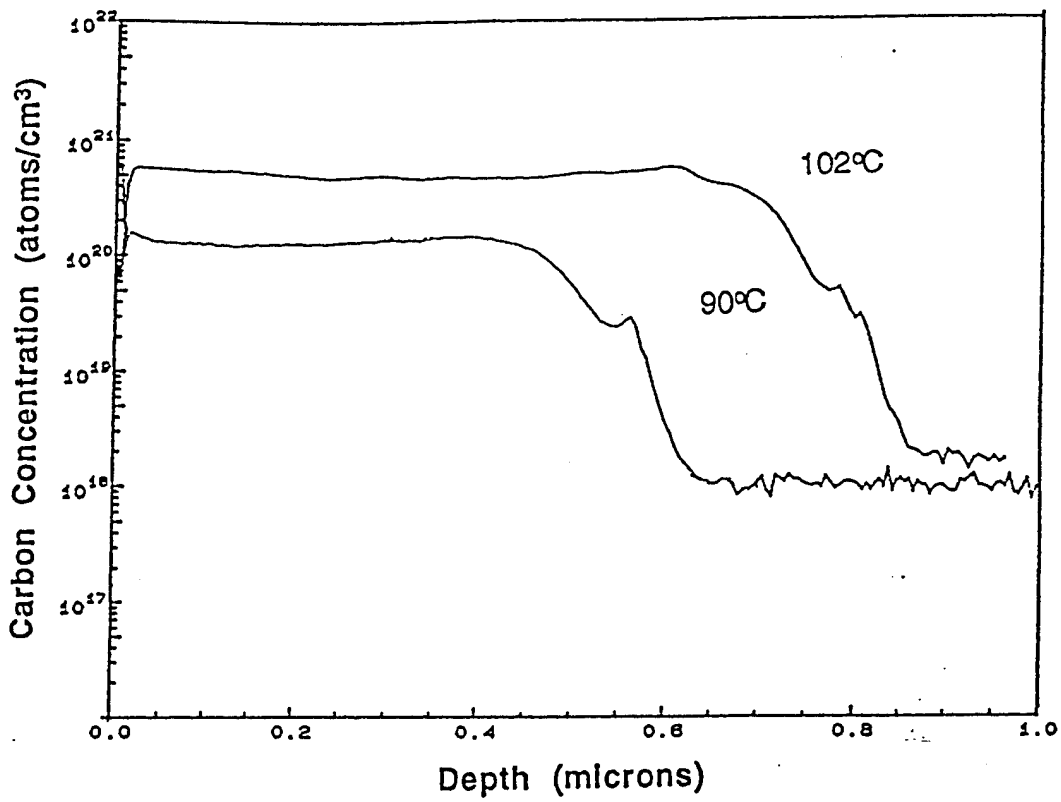






Rogers, Figure 7





Rogers, Figure 9

