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13. ABSTRACT *(Maximum 200 Words)*

The goal of this investigation was to determine the role of co-dopants in the effort to obtain useful EL from Er doped Si devices. One unforeseen difficulty was the essential role that co-dopants played in the simple epitaxial growth of Er doped Si material. Without co-dopants, the Er introduced during growth, segregates to the growth surface and prevents single crystal formation. It was decided to produce films with varying O and/or O/C co-doping concentrations. This material was found to produce a strong PL response as hoped. The next step was to produce a device that incorporated this material into the vicinity of the metallurgical junction that defined the PN junction. First it was necessary to prove that our overall process could be used to fabricate working PN junctions with large reverse bias voltages. This was not automatic, and it was necessary to develop a process that would reproducibly give diodes with high reverse bias voltages. This work was more involved than originally anticipated and actually resulted in a patent application of the process. Several Er doped Si diodes were fabricated from material that produced strong PL signals, however no EL was observed. It was concluded that due to device geometry, the EL signal was to low for our low efficiency detector to see.

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Sincerely,

Walter J. Varhue

Walter J. Varhue

REPORT DOCUMENTATION PAGE (SF298)
(Continuation Sheet)

Statement of Problem Studied:

The purpose of this investigation was to develop a process of producing Er doped Si material and devices in a form that could generate useful light emission. The original thought was that the highly sought after 1.54 micron infrared emission could be obtained as the result of a direct energetic electron impact excitation. The goal was to place the Er ion, the presumed light emitting center, in the depletion region of a reverse biased diode. To sustain a high reverse bias field in the depletion region of this diode, a properly functioning Si diode had to be produced. The fabrication of a properly functioning diode requires the ability to produce 1. high quality epitaxial Si material and 2. electronically neutral interfaces. Along with this properly functioning reverse biased PN junction diode, a high concentration of Er centers are required to be placed in the junctions depletion region. The greater the performance of the reverse biased PN junction, the greater the likelihood to obtain the free carrier acceleration required to observe the Er emission.

Summary of the Most Important Results:

In the first analysis, the goal to produce an Er doped Si device capable of yielding practical and efficient levels of IR radiation, requires that two general steps be achieved. A brief description of these steps are as follows; 1. The ability to grow high quality epitaxial Si films doped with a high concentration of Er. and 2. The ability to fabricate a properly functioning PN junction diode that can sustain a high reverse bias field, sufficient to allow avalanche breakdown.

1. Growth of Epitaxial Si Thin Films Doped with Er.

The initial intention was to deposit Si films doped with Er metal atoms. The original thought was that the co-dopants e.g. O,N,B or F typically used to produce optically active Er photoluminescent centers in Si would only degrade thin film quality and reduce the mean free path of accelerated electrons. Further it was postulated that the co-dopants would not be required for the emission of light by this direct impact excitation mechanism. The co-dopants are necessary for the exciton mediated process such as photoluminescence and electroluminescence. The Er would be added to the Si lattice coincident with film growth via a co-sputtering process utilizing a RF driven Er metal target. It was quickly found however that the Er dopant added during growth was segregating to the surface of the film and poisoning further crystal growth. Proper growth and incorporation were achieved only by including small amounts of oxygen (10^{18} – 10^{20} cm^{-3}) added during deposition. A Secondary Ion Mass Spectrometry (SIMS) trace is shown to prove this point in Figure 1. It is assumed that the highly reactive Er ion reacts with oxygen on the Si surface before it is covered over in the deposition process. The same result was achieved by adding carbon via the addition of methane or fluorine with the operation of a homemade effusion cell. Our goal in making these different attempts was to obtain the highest crystalline quality material with the most intense emission. The PL measurements

were made with a set up that utilized a thermoelectrically cooled Ge diode detector. This detector was sufficiently sensitive to measure the PL generated by the excitation initiated by a 100 mW Ar laser. The PL spectra of oxygen and fluorine co-doped epitaxially grown Si material is shown in Figure 2. a and b. The most consistent results were obtained for material co-doped with oxygen and therefore the diodes were constructed with this material combination.

2. Fabrication of PN Junction Diode:

Although in principle simple, the fabrication of a properly functioning PN junction diode capable of sustaining a high reverse bias potential is difficult in practice to achieve. Along with this criteria, an additional requirement is that the process be performed at low temperatures to maximize the concentration of Er centers. Higher process temperatures would result in the precipitation of Er silicides which are known to be optically inactive. Further the precipitation of this silicide phase would limit the electron's mean free path and inhibit avalanche multiplication.

Low temperature Si growth processes exist such as the UHV-CVD at (600 –800 ^{o}C) that is used so widely in industry today. However this process by it nature would not permit the incorporation of large concentrations of Er and therefore would be impractical for this application. The greatest chance of obtaining a high Er concentration is to use a non-equilibrium process such as plasma enhanced chemical vapor deposition. The addition of Er to the Si epitaxial film produces at least two physical effects. Along with the Er dopant's desired optical properties when alloyed with a co-dopant, it also acts as an n-type electrical dopant in Si. The plan was to place the Er dopant in the depletion region, on the lower doped n-type side. The lower doping level will extend the length of this region and therefore increase the level of avalanche multiplication. In this region of the diode, Er is the only extrinsic dopant added. The production of a good ohmic contact to the n-type region is facilitated by heavily doping the last 200 angstroms of this material with an n-type dopant. In this investigation both Er and Sb were used for this purpose.

The substrates used were moderately B doped (5×10^{19} cm^{-3}) p-type Si (100) wafers. The metallurgical junction of the diode was formed at the wafer surface with the initiation of the n-type (Er doped) film growth. Initially, all the fabricated diodes broke down at low reverse bias potentials. All indications were that the devices were suffering from reverse bias breakdown as a result of trap assisted tunneling at the substrate interface. On a further investigation of the literature it was found that there was little previous work attempting to form diodes that placed the metallurgical junction at the initial substrate interface. Epitaxially formed diodes are typically fabricated by first depositing a region of the same dopant type as the substrate followed by a switch to the other dopant type after high quality growth of the layer has been established. The purpose of this step is to reduce the possibility of incorporating original surface defects into the metallurgical junction of the device which facilitates tunneling breakdown.

It would however be very convinent for this and other applications to be able to form PN junction diodes with their metallurgical junctions located at the original wafer surface. This prospect is particularly difficult for low temperature processing

as was attempted here. Higher temperature CVD processes typically include a 900 °C hydrogen pre-bake which can effectively remove oxygen and carbon contaminants from the substrate surface. One of the advantages of low temperature processing however is the prospect of forming a super abrupt junction. In the past, considerable effort has been expended investigating the preparation of the substrate surface for future epitaxial growth. It has been shown in numerous investigations that an *in-situ* hydrogen plasma cleaning step is required to remove both oxygen and carbon from the growth surface to permit future epitaxial growth. Although this was also the case in this investigation, it was found that the plasma clean damages the growth surface and makes it impossible to form properly functioning diodes.

This problem was remedied by developing an alternative cleaning process that included an *ex-situ* ozone cleaning step to remove carbon contamination. This process produced the break through that was need in fabricating PN junction diodes with large reverse bias breakdown potentials. The results of this work were written up as a patent disclosure that was recently awarded. A comparison of the I-V curves resulting from several of the devices fabricated using the different cleaning processes is shown in Figure 3.0. Additional I-V characteristic curves are presented in Figure 4.0 for diodes doped with three different levels Er/O concentrations. When operating the optimum devices in the reverse bias condition, visible white light was visible to the naked eye in a darkened room. The origin of this white light is the recombination of accelerated electrons, shifted in momentum space to coincide with the maximum of the valance band peak.

Light Emission:

In spite of these encouraging results, the 1.54 micron emission was not successfully recorded by our detection system. The reason for this failure was undoubtedly the sensitivity of the detection system. All of the results reported in the literature utilized a highly sensitive hyper pure Ge detector provided by the former North Coast Corporation. The cost and availability of the detector made it impractical to make this measurement. The question might arise as to how our system could clearly detect the PL spectra from our Er doped films but not from our diode structure. The answer lies in the theoretical volume of the optically pumped versus that of the electrically pumped diode source. The beam diameter of the Ar laser was on the order of a millimeter and the penetration and diffusion length of the generated excitons was microns. Although small, this is enormous in comparison to that volume expected from the reverse biased diode. That volume was set by the width of the depletion region and the area of the electrode contact. This volume was effectively reduced further by the shadowing effect of the metal contact. An attempt was made to limit this effect by using a dounut shaped electrical contact. The ratio of emitting volume was estimated to be less than a thousand of that used in the PL experiment. In conclusion the intensity of useful light emission is small and will require additional innovations would be required to make this a practical IR emission source.

(6.) Listing of all Publications:

a.) Peer-Reviewed Journals:

1. S. G. Reidy, W. J. Varhue, E. Adams, and M. Lavoie, "Electrical Properties of PN Junctions Formed by Plasma Enhanced Epitaxial Growth", J. of Applied Physics, to be published January 2002.

c.) Papers Presented at Meetings:

1. T. H. Nguyen, S. G. Reidy, W. J. Varhue, E. Adams, S. Mongeon and M. Lavoie, "High Deposition Rate Epitaxial Si and SiGe Films Grown by ECRPECVD", American Association for Crystal Growth, Burligton VT, August 2001.

d.) Manuscript Submitted:

1. S. G. Reidy, W. J. Varhue, E. Adams, S. Mongeon and M. Lavoie, "Ex-situ Surface Preparation in the Growth of Epitaxial Silicon Films by Plasma Enhanced Chemical Vapor Deposition", Journal of Electronic Materials. (under review).

(7.) List of all Participating Scientific Personnel showing an Advanced Degree Earned while Employed on the Project:

Sean G. Reidy earned a Ph.D. in Materials Science and defended his thesis in June 2001 . The title of his dissertation was "Plasma Enhanced Processing of Silicon for Electronic and Optical Device Applications".

(8.) Report of Inventions by Title:

1. Structure and Method for Abrupt PN Junction Diode Formed Using Chemical Vapor Deposition Processing. Allowed Nov. 2001.
2. Divisional, Structure and Method for Abrupt PN Junction Diode Formed Using Chemical Vapor Deposition Processing. In process of filing.

(10.) Appendixes: Figures

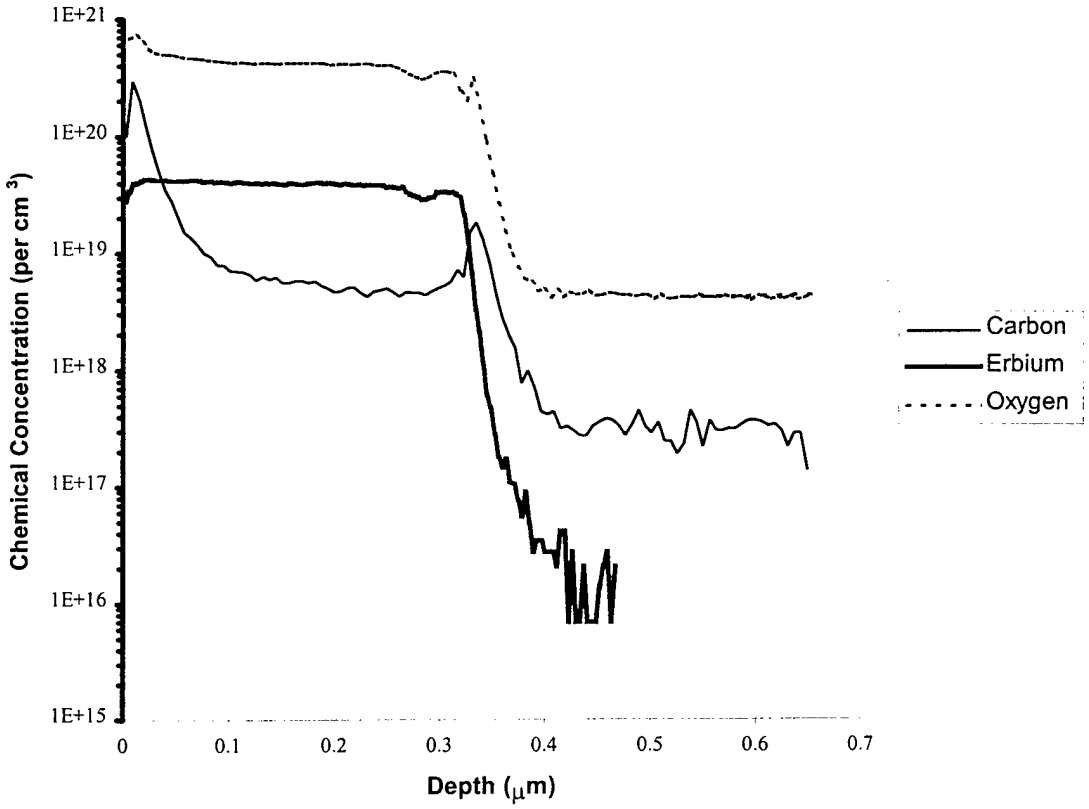
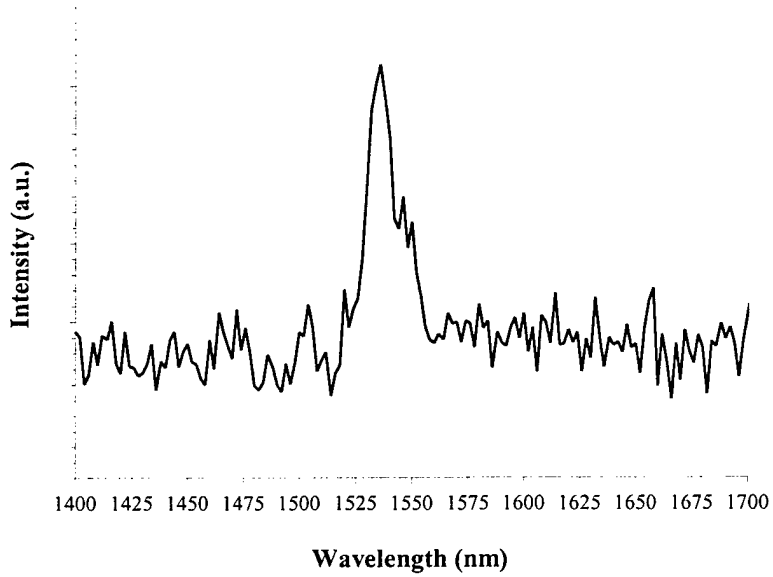


Figure 1. Secondary ion mass spectrometry result for a film doped with erbium and oxygen by reactive sputtering during plasma enhanced chemical vapor deposition.



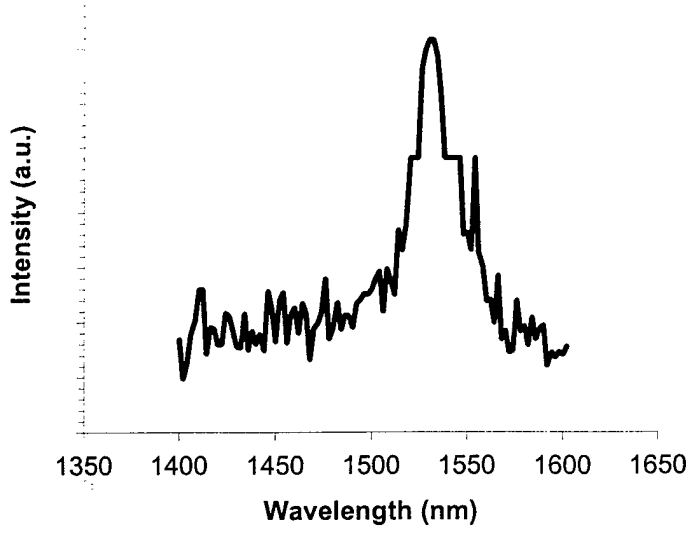


Figure 2. Photoluminescence spectra for a Si:Er/O co-doped film (top) and a lightly doped Si:Er/F film (bottom).

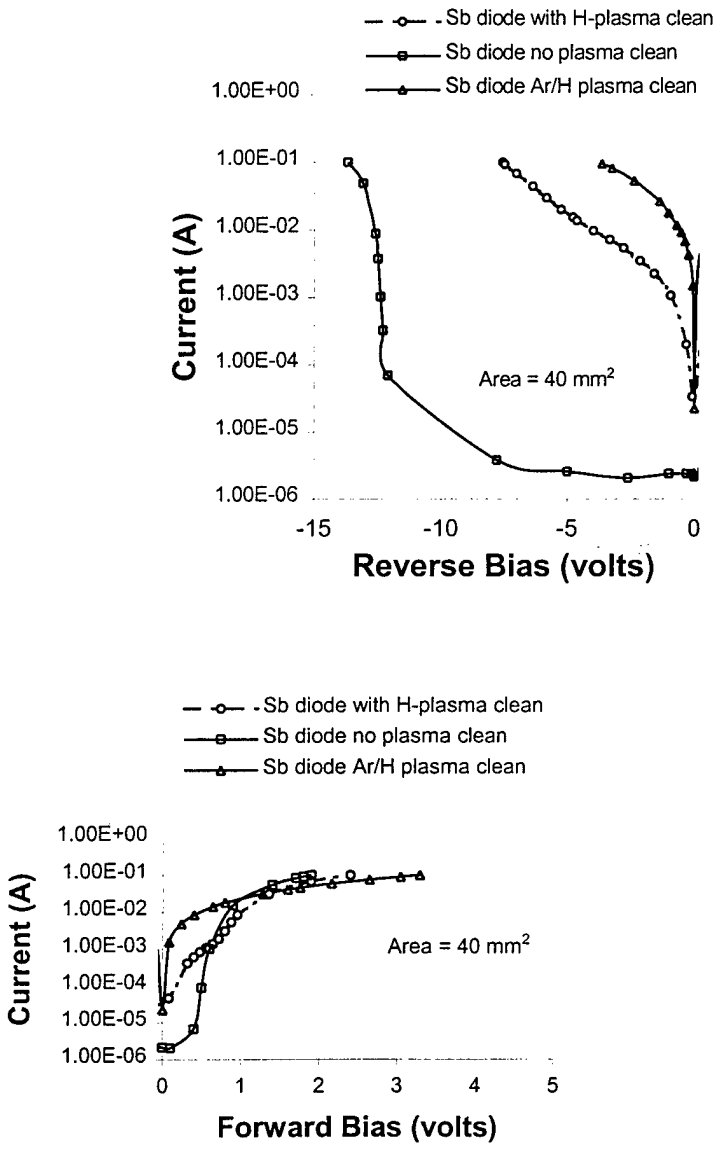


Figure 3. Reverse and forward bias I-V characteristic curves for diodes fabricated with three different surface preparation methods.

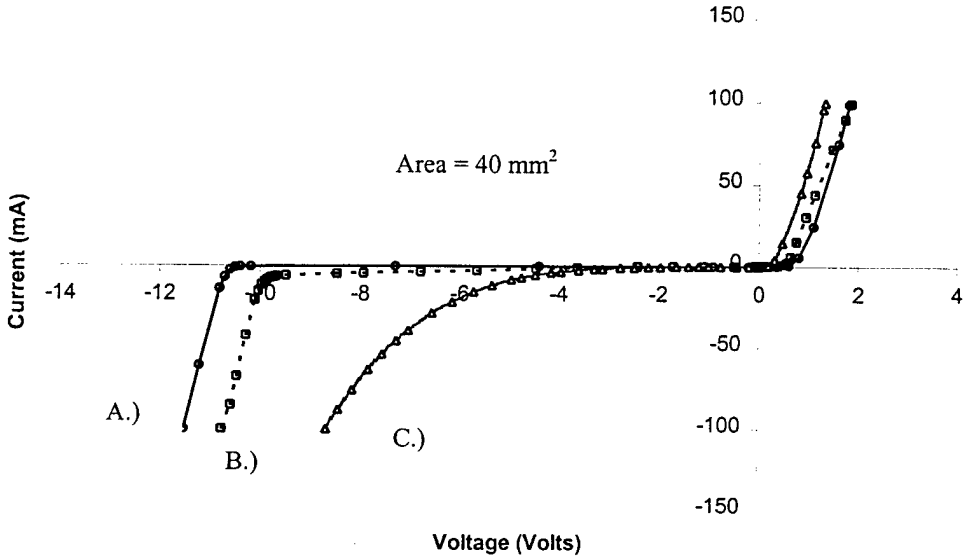


Figure 4. IV characteristic curves of an Si:Er/O diodes. The junction breakdown at approximately A.) 11, B.) 10, and C.) 7 V indicates an electron concentration of approximately 0.5 x 10^{17}/cm^3 , 2 x 10^{17}/cm^3, and 8 x 10^{17}/ cm^3 in the Er/O doped thin film respectively.