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Pulsed XeCl laser annealing of ZnS:Mn thin films

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We describe pulsed XeCl (308 nm) laser annealing of ZnS thin films implanted with Mn ions and deposited onto single-crystal Si substrates. Successful annealing of the films only occurs when the specimens are held under inert gas pressure of several atmospheres during the laser pulse in order to obtain melting and regrowth of the films without appreciable vaporization. Typically, specimens annealed under 90 pounds per square inch, gauge (psig) of Ne at laser energy densities in excess of ~ 0.8 J cm^{-2} exhibit a higher Mn photoluminescence signal than comparable samples thermally annealed at 500 °C, the difference being a factor of ~ 2 at 2.5 J cm^{-2}. Evidence for increased crystallinity in these specimens after laser annealing has also been obtained.

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Thin films of ZnS doped with Mn show promise for fabricating light emitting devices.[1] In general the specimens require a post-deposition annealing treatment in order to activate the Mn luminescent centers, this being especially true when the Mn ions are introduced by ion implantation; the fact that this technique produces considerable structural damage in the host material is well known. Conventional methods of annealing by heating the entire specimen to several hundred °C often have undesirable consequences and considerable interest has recently been generated in an alternative annealing procedure employing pulsed laser radiation. This technique has largely been used for annealing Si and the group III-V semiconductors,[2,3] there being very little work published on the pulsed laser annealing of group II-VI semiconductors.[4,5] In this letter we report, to our knowledge, the first successful pulsed laser annealing experiments on Mn-implanted ZnS films deposited onto single-crystal Si substrates. A preliminary presentation of some of these results has recently been made.[6]

The ZnS films were deposited onto *n*-type (100) single-crystal Si substrates either by condensation of vapor sublimed from solid ZnS source material in a diffusion pumped ultrahigh vacuum system or by rf sputtering from a solid ZnS target in an argon atmosphere. Details of sample fabrication will be published elsewhere. Silicon was chosen as the substrate material because its close lattice match with ZnS affords the possibility of growing epitaxial films[7,8] and possible epitaxial regrowth after laser annealing. Also the possibility exists of fabricating integrated electroluminescent displays. In this report, only data obtained on the sputtered specimens will be presented. These were polycrystalline in nature and typically 2000 Å thick. Mn ions with an energy of 300 keV were implanted into the films (at A. E. R. E., Harwell) at a dose of 3×10^{15} ions cm^{-2} (corresponding to a concentration of ~ 0.3 at. %); at this implantation energy the range plus straggle of Mn in ZnS is ~ 2200 Å.[9]

The laser annealing experiments were carried out with an electron beam pumped XeCl laser[10] operating at 308 nm. At this wavelength the absorption coefficient of ZnS films is $\sim 2\times 10^5$ cm^{-1} and thus efficient coupling of the laser beam with the films can be obtained. The laser pulses were gaussian in profile with typical widths of ~ 40-ns FWHM and maximum energies of ~ 0.75 J over a spot size of 38-mm diameter. Energy densities of up to ~ 3 J cm^{-2} could be obtained for the annealing experiments by focussing of the beam. From beam profile measurements[6] the spatial uniformity of the radiation over its diameter was estimated to be $\sim 10\%$. In fact the uniformity over the annealed areas, even when the beam was focussed down, was better than this figure as only a fraction of the beam area was utilized. During annealing the specimens were either in air or in an inert gas (Ne) environment in a pressure vessel capable of being pressurized to 100 pounds per square inch, gauge (psig).

After laser annealing, the orange Mn photoluminescence (PL) emission from the irradiated regions was examined at room temperature and used as a probe to monitor the annealing process, this PL emission being totally absent in nonannealed specimens. The PL was excited by chopped (117 Hz) 320-nm radiation from an Oriel 7240 grating monochromator with a 150-W Xe arc lamp source and analyzed by a similar monochromator interfaced to a cooled photomultiplier unit whose output was fed to a lock-in amplifier and a chart recorder. An examination was also made of the structure of the annealed areas using reflection high energy electron diffraction (RHEED). Composition measurements using Rutherford backscattering showed no measurable change in the Zn to S ratio of the films after laser irradiation and will not be discussed further.

The most significant result to emerge from the present study is the fact that for successful laser annealing of the ZnS:Mn films it is essential to carry out the experiments with the specimens under inert gas pressure. In air at atmospheric pressure, appreciable vaporization of ZnS occurs from the irradiated regions above energy densities of ~ 0.2–0.3 J cm^{-2}, with significant cracking of the remaining film material at the highest energy densities.[5] Furthermore, the atmospherically annealed films show no PL below ~ 0.8 J cm^{-2} and only a very weak signal above this figure (see Fig. 1). In contrast, Fig. 1 depicts the variation of the PL peak intensity with laser energy density when the annealing is

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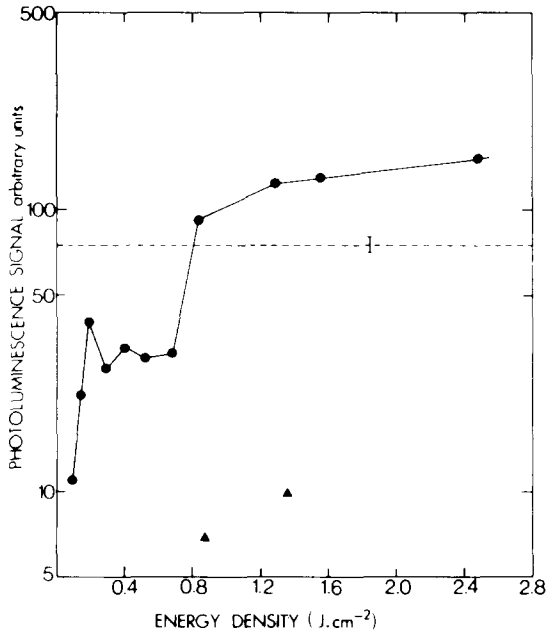


FIG. 1. Mn peak PL intensity vs laser energy density for films annealed under 90 psig of Ne (●) and in air (▲). The horizontal dotted line represents the luminescence obtained under identical measurement conditions from similar specimens thermally annealed under vacuum at 500 °C for ~2 h.

carried out under a gas pressure of 90 psig. A significant PL signal is observed, particularly at the higher energy densities. In fact above ~0.8 J cm^{-2}, the luminescence from the laser annealed specimens exceeds that from comparable thermally annealed films, the difference being a factor of ~2 at 2.5 J cm^{-2} (see Fig. 1). Also, under these conditions, there is no measurable loss of material from the annealed areas below ~1–1.2 J cm^{-2} although some material is lost at higher energy densities. Further evidence showing the importance of annealing under pressure is given in Fig. 2 for 2.8-J cm^{-2} anneals. Although the data is rather limited, the variation of PL with gas pressure becomes less pronounced above pressures of 40–50 psig.

Typical PL spectra showing the Mn emission band for a film laser annealed at 2.5 J cm^{-2} under 90 psig of Ne and a similar specimen thermally annealed under the conditions

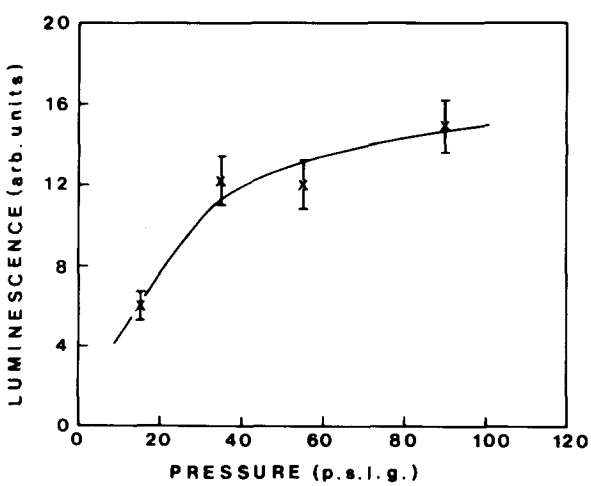


FIG. 2. Mn peak PL intensity vs ambient Ne pressure during 2.8-J cm^{-2} laser anneals.

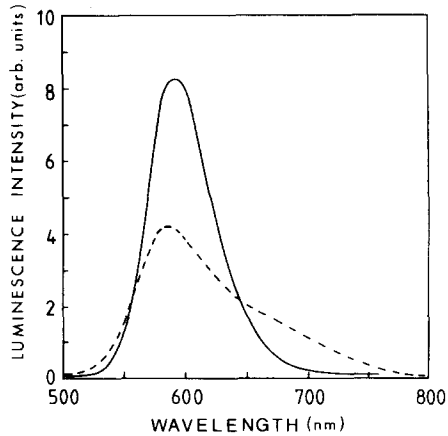
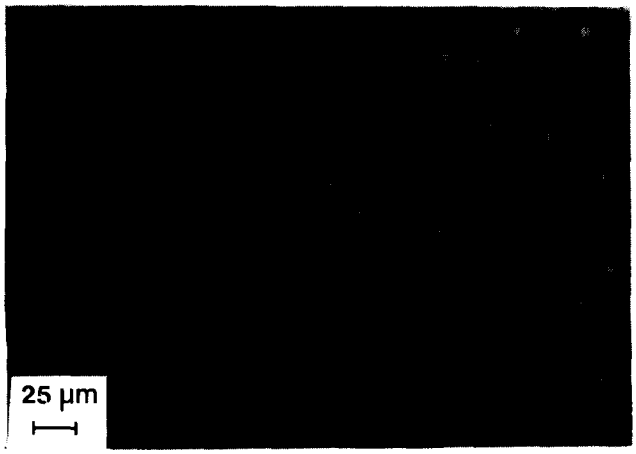


FIG. 3. Photoluminescence spectra for a sample laser annealed at 2.5 J cm^{-2} (solid line) and thermally annealed under the conditions given in Fig. 2 (dotted line). The spectra are uncorrected for system response.

noted in Fig. 1 are shown in Fig. 3. The spectra were recorded under identical measurement conditions and exhibit the above mentioned difference in the luminescence intensity. Additionally there is a pronounced difference in the peak shapes, also the emission from the thermally annealed specimen peaks at 5860 Å as opposed to 5925 Å for the laser annealed emission. Further work is necessary to account for these differences and a relevant discussion will be presented elsewhere.

An optical micrograph and a RHEED pattern for a film annealed at 2.5 J cm^{-2} under 90 psig of Ne are shown in Fig. 4. The structure in Fig. 4(a) and the spots in the diffraction pattern appear only after annealing and indicate increased crystallinity of the films after laser irradiation. In fact, at 90 psig, similar features are present in all the specimens annealed above ~0.6–0.8 J cm^{-2} and become more pronounced with annealing energy density. This is also true for the specimens whose data is presented in Fig. 2 for anneals above pressures of ~40 psig. These observations, together with the rippled surface appearance of some specimens under Nomarski interference microscopy, imply melting of the ZnS:Mn layers during irradiation.

At the present time much additional work remains to be done to clarify the various aspects of this study. Nevertheless, the initial and tentative results presented above show the important role played by the pressure under which the laser annealing is carried out. A possible explanation for this emerges from the fact that ZnS has an appreciable vapor pressure of ~3–4 atmospheres at 1830 °C (its melting point under 150 psig of Ar[11]) and cannot be melted at all much below ambient pressures of ~50 psig.[11] Hence only under sufficient pressure can successful laser annealing occur, most probably by melting and regrowth of the layers with concomitant redistribution of the Mn ions and an improvement in the film crystallinity; both of the latter factors could be responsible for the improved PL emission.[12] These concepts are supported by the data of Fig. 2 and the results presented in Fig. 1, coupled with the initial structural investigations (see Fig. 4), imply a possible melting threshold in the region of ~0.6–0.8 J cm^{-2} under 90 psig of Ne. However further work is necessary to confirm this.



(a)

(b)

FIG. 4. (a) Optical micrograph and (b) RHEED pattern taken at 80 kV for a specimen laser annealed at 2.5 J cm^{-2} under 90 psig of Ne.

In conclusion we have presented evidence showing that ZnS:Mn layers deposited onto Si substrates can be laser annealed, but only under pressure; even the great speed of the pulsed laser annealing process[2,3] cannot prevent significant and detrimental vaporization of the material under atmospheric conditions. This result may have applicability to the laser annealing of other group II-VI semiconductors as well as other materials. The slight loss of material which still occurs under pressure for the highest energy density anneals suggests that pressures in excess of ~ 100 psig may have to be employed.

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[1] J. Kirton, in *Handbook in Semiconductors*, edited by C. Hilsum (North-Holland, Amsterdam, 1981), Vol. 4, pp. 665–690.
[2] *Laser-Solid Interactions and Laser Processing—1978*, edited by S. D. Ferris, H. J. Leamy, and J. M. Poate (AIP, New York, 1979).
[3] *Laser and Electron Beam Processing of Materials*, edited by C. W. White and P. S. Peercy (Academic, New York, 1980).
[4] C. B. Edwards and H. S. Reehal, in Annual Report to the Laser Facility Committee, SERC Rutherford and Appleton Laboratories, 1981, pp. 2.17–2.18 (unpublished).
[5] F. J. Bryant, D. M. Staudte, and P. R. Jaffery, Solid State Commun. **37**, 625 (1981).
[6] H. S. Reehal, C. B. Edwards, J. M. Gallego, and C. B. Thomas, presented at the Fifth National Quantum Electronics Conference, Hull University, Hull, September 1981 (to be published by Wiley).
[7] P. L. Jones, C. N. W. Litting, D. E. Mason, and V. A. Williams, J. Phys. D **1**, 283 (1968).
[8] T. G. R. Rawlins, J. Mater. Sci. **5**, 881 (1970).
[9] J. Lindhard, M. Scharff, and H. E. Schiott, K. Dan. Vidensk. Sels. Mat-Fys. Medd. **33**, 14 (1963).
[10] C. B. Edwards, F. O'Neill, and M. J. Shaw, Appl. Phys. Lett. **36**, 617 (1980).
[11] A. Addamiano and P. A. Dell, J. Phys. Chem. **61**, 1020 (1957).
[12] J. M. Hurd and C. N. King, J. Electron. Mater. **8**, 879 (1979).