

LRP 478/93

July 1993

ROOM TEMPERATURE VISIBLE
PHOTOLUMINESCENCE FROM SILICON
PARTICULATES PREPARED IN A RF
SILANE PLASMA

J. Dutta, J.-L. Dorier, Ch. Hollenstein,
A.A. Howling, L. Sansonnens, Ch. Nieswand,
A. Fasoli & T. Stoto

submitted for publication to Appl. Phys. Lett.

**ROOM TEMPERATURE VISIBLE PHOTOLUMINESCENCE
FROM SILICON PARTICULATES PREPARED IN A RF
SILANE PLASMA**

J. Dutta, J.-L. Dorier, Ch. Hollenstein, A. A. Howling,

L. Sansonnens, C. Niswand and A. Fasoli

Centre de Recherches en Physique des Plasmas
Swiss Federal Institute of Technology
21 Av. des Bains, CH-1007 Lausanne
SWITZERLAND

&

T. Stoto

Laboratoire de Physique des solides semi-cristallins- IGA/DP
Swiss Federal Institute of Technology
CH-1015 Lausanne
SWITZERLAND

(PACS no.: 78.55.-m, 81.15.Gh, 81.20.-Ev, 52.70.-m, 61.50.-f)

ABSTRACT

Visible photoluminescence at room temperature has been observed in silicon particulates prepared in a silane rf plasma. Photoluminescence measurements were carried out on 'as-deposited' particulates and also on particulates suspended in the plasma during processing. The photoluminescence spectrum peaks at 730 nm and 780 nm (using the 488 nm line of an Ar⁺ ion laser), partly covering the visible region, for some of the particulates suspended in the plasma and for the others collected on a steel plate, respectively. It is suggested that the photoluminescence originates from nanocrystallites of silicon formed in these particulates. The in situ photoluminescence measurements in processing plasmas could serve as a diagnostic tool for plasmas involving particulate formation.

Ever since Canham et. al.¹ demonstrated the viability of preparing visible light-emitting silicon materials by electrochemical means, there has been a strong interest in these types of materials as they are promising for a wide range of applications in opto-electronic devices. Many groups have since repeated the experiment and have successfully prepared porous silicon materials.²⁻⁴ Canham et. al.¹ originally explained their results in terms of quantum confinement of the electrons resulting in band-gap enhancement in the silicon wires which are formed due to the electrochemical etching. However, Stutzmann et. al.⁴ proposed that the visible photoluminescence originates from siloxene-type compounds formed during the electrochemical etching of silicon because these compounds have a broad photoluminescence signal in the visible region, quite similar to the porous silicon photoluminescence spectra. Although it is now generally agreed that quantum confinement of the electrons increases the optical gap of porous silicon which leads to the visible light emission, limitations in the sample preparation techniques still do not allow the oxygen-related effects to be completely eliminated.

Several other attempts to prepare silicon materials by various techniques have shed further light on the origin of the visible (above gap) photoluminescence in nano-crystalline silicon.⁵⁻¹¹ As early as 1983, Wolford et. al.⁶ showed the possibility of achieving efficient visible light emission at room temperature from silicon particulates prepared by plasma enhanced chemical vapour deposition from disilane. They interpreted their results in terms of

hydrogen rich regions being responsible for the luminescence. However, Takagi et. al.⁷ have recently shown that the particulates formed from a silane plasma by a microwave discharge consist of nano-crystallites of silicon embedded in an amorphous matrix. These particulates were found to photoluminesce in the visible region and the spectra showed quantum size effects. In separate studies, Furukawa et. al.,⁸ Morisaki et. al.,⁹ Brus et. al.¹⁰ and Kawaguchi et. al.¹¹ have reported room temperature visible light emission from silicon particulates prepared by sputtering of silicon in hydrogen, evaporation of silicon powder, pyrolysis of silane and by the dissociation of silane by ultraviolet irradiation, respectively. In all of these cases, however, the photoluminescence measurements were carried out in the ambient or the particulates were oxidised and hence oxygen-related effects can still not be clearly discounted.

In this letter we report on the preparation of room temperature photoluminescing particulates of silicon by a Plasma Enhanced Chemical Vapour Deposition (PECVD) technique. Photoluminescence measurements were carried out on 'as-deposited' particulates and, for the first time to our knowledge, on particulates suspended in the plasma, in conditions with minimal oxygen contamination. We observe that these particulates contains nano-sized crystals and suggest that the room temperature photoluminescence originates due to band gap enhancement in these crystallites.

The silicon particulates were prepared in a PECVD system evacuated to less than 10^{-6} Torr prior to processing. These

particulates are similar to the ones generally formed during hydrogenated amorphous silicon deposition.¹² The capacitively-coupled, parallel plate electrodes were driven by a rf frequency of 30 MHz. The source gas used for the deposition was silane (flow rate 30 sccm) which was dissociated by a rf input power of 6-10 W. The processing pressure was kept constant at 0.1 Torr and the reactor was maintained at room temperature. In figure 1 we have schematically represented the deposition system and the measurement set-up; a detailed description of the reactor is available elsewhere.¹² Samples were either deposited directly on the electrodes, or were collected on stainless steel plates (2 cm x 3 cm) placed outside the edge of the plasma ('Position B', Figure 1). In some other runs, particulates were deposited onto Corning 7059 glass substrates, which were placed on the top electrode. The plasma was stopped after the stainless steel plates were completely covered by the particulates and the silane in the reactor was evacuated by a turbomolecular pump. The sample was then adjusted to 'Position A' (Figure 1) and irradiated at 45° through a band pass filter (488 nm, band width 9 nm) by an Ar⁺ ion laser (power density ~ 100 mW/cm²) in vacuum (less than 10⁻⁵ Torr). The photoluminescence signal was detected through a coloured high-pass filter (edge position at 530 nm) by a spectrometer coupled to an Optical Multichannel Analyser (OMA). The recorded spectra were corrected for the spectral response of the detection system with respect to a standard calibration source. For the photoluminescence measurements of the particulates suspended in the plasma a similar arrangement was used except that the background plasma emission was subtracted from the measured signal. For these measurements

light from a small volume around 'Position A' was collected and analysed by the OMA.

In Figure 2 we have shown the normalised photoluminescence signal from three different samples, two collected outside the plasma (i.e. in 'Position B' of Figure 1), and the other deposited on a glass substrate placed on the upper electrode. We noticed that the particulates collected on the electrodes always showed a photoluminescence peak beyond 900 nm (i.e. beyond the detection limit of our OMA). However, the particulates collected outside the plasma showed a clear photoluminescence with peaks at ~780 nm and ~810 nm (Figure 2), partly covering the visible region, which is very similar to the photoluminescence spectra from unoxidised silicon particulates reported by others.⁷⁻⁹ The sample luminescing at 780 nm was collected further away from the plasma edge compared to the other, and possibly due to the differential pumping of the particulates (depending on their sizes) they have different size distributions. The major problem in these experiments was inefficient collection of particulates on the probe. Special attention needs to be given to solve this problem of particulate collection.

In Figure 3 we show a typical spectrum of the photoluminescence signal which peaks at ~730 nm from particulates suspended in the plasma. This photoluminescence is visible to the naked eye using a 530 nm high pass filter to cut off the scattered laser light. It is relevant to mention here that observation of the

photoluminescence signal from particulates suspended in the plasma is only possible after proper conditioning of the reactor. We do not yet completely understand the evolution and dynamics of the photoluminescing particulates in silane plasmas. Only those particulates suspended in a silane plasma near the plasma/sheath boundary photoluminesce. The processes leading to the formation of these photoluminescing particulates merit further investigation.

Since all the processing and measurements were carried out in conditions where minimal oxygen contamination is possible, contributions to the photoluminescence signal from oxide-like phases, if any, should be negligible. Since we observe the photoluminescence from particulates during their formation in the plasma, this also suggests that the origin of the room temperature photoluminescence in the particulates is probably not from any oxide-like phases of silicon, as some researchers have suggested for the porous silicon materials.⁴ Although it is difficult to comment at this stage on the possible effects of post-oxidation of these particulates on the photoluminescence properties, it does not seem a necessary condition for achieving room temperature photoluminescence. Oxidation of the particulates might in retrospect lead to the passivation of non-radiative centres, which could lead to higher luminescence efficiencies.⁹

In figure 4 we have shown a typical high resolution transmission electron micrograph of a particulate collected on a carbon-coated copper grid placed on the bottom electrode. In these

particulates we observe that silicon crystallites with a mean size of about 70 Å are embedded in an amorphous matrix. Although we have not yet made any detailed structural characterisation of these crystallites, the transmission micrograph of these particulates looks very similar to the other silicon nano-crystallite structures reported in the last couple of years.⁷⁻¹¹ Theoretical calculations and experimental observations have shown that crystallites of these dimensions show quantum confinement effects leading to an effective increase in the band gap.¹³⁻¹⁶ We believe that the room temperature visible photoluminescence we observe originates from band-gap enhancement in silicon nano-crystallites present in these particulates.

It may be interesting to add here a few comments on the formation of the crystallites in these particulates. According to the calculations of Brus,¹⁷ the crystallisation energy in clusters is much reduced compared to the bulk. Particulates formed in the plasma due to polymerisation can be heated by the plasma and this could give sufficient energy to melt these particulates,¹⁸ which by heat exchange processes can quench to form the nano-crystallites. The particulates collected in the plasma (at the top or the bottom electrodes) which luminesce with a peak beyond 900 nm are possibly of larger size. For a better understanding of the particulate/crystallite formation however, it is necessary to carry out a detailed systematic structural analysis of these particulates formed under different plasma conditions.

In conclusion, we have demonstrated a new processing technique for the preparation of nano-crystalline silicon and have shown that this material photoluminesces in the visible region at room temperature. Since all the processing and subsequent measurements were carried in conditions with minimal oxygen contamination, and since we also observe photoluminescence from the particulates suspended in the plasma during processing, the photoluminescence signal probably does not originate from any oxide-like phases of silicon. We believe that the room temperature visible photoluminescence in the silicon particulates results from the band gap enhancement due to quantum confinement in the nano-sized crystals embedded in the particulates. In situ photoluminescence measurements during plasma processing could serve as an interesting diagnostic tool for processing plasmas involving particulate formation.^{19,20} Finally, since the PECVD process is a well-known and commercially well-developed process, possibilities of using this technique for suitable preparation of particulates will be fairly simple and thus this processing technique presents further possibilities for future applications towards the fabrication of nano-sized structures.

ACKNOWLEDGEMENTS

We would like to thank Dr. E. F. Steigmeier of PSI, Zürich for his interest in this work. We also thank Prof. L. Zuppiroli for proposing the initial measurements which led to the development of this program. The work was supported by the Swiss Federal Optics Priority Program and funded by Swiss Federal Grants from EF-REN (91)31 and BBW.EG (91)3 (for BRITE/EURAM contract BE- 4529-90).

References

1. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).
2. V. Lehmann and U. Gösele, *Appl. Phys. Lett.* **58**, 856 (1991).
3. M. A. Tischler, R. T. Collins, J. H. Stathis and J. C. Tsang, *Appl. Phys. Lett.* **60**, 639 (1992).
4. M. Stutzmann, J. Weber, M. S. Brandt, H. D. Fuchs, M. Rosenbauer, P. Deak, A. Höpner and A. Breitschwerdt, *Advances in Solid State Physics, Festkörperprobleme* **32**, 179 (1992).
5. E. F. Steigmeier, H. Auderset and B. Delley, *Physica Scripta* **T45**, 305 (1992)
6. D. J. Wolford, J. A. Reimer and B. A. Scott, *Appl. Phys. Lett.* **42**, 369 (1983).
7. H. Takagi, H. Ogawa, Y. Yamazaki, A. Ishizaki and T. Nakagiri, *Appl. Phys. Lett.* **56**, 2379 (1990).
8. S. Furukawa and T. Miyasato, *Phys. Rev.* **B38**, 5726 (1988).
9. H. Morisaki, F. W. Ping, H. Ono and K. Yazawa, *J. Appl. Phys.* **70**, 1869 (1991).
10. L. Brus, K. Littau, A. Muller and P. Szajowski, *Bull. Am. Phys. Soc.* **37**, 719 (1992).
11. I. Kawaguchi and S. Miyazima, *Bull. Am. Phys. Soc.* **37**, 719 (1992).
12. J.-L. Dorier, Ch. Hollenstein, A. A. Howling and U. Kroll, *J. Vac. Sci. Technol.* **A10**, 1048 (1992).
13. A. J. Read, R. J. Needs, K. J. Nash, L. T. Canham, P. D. J. Calcott and A. Qteish, *Phys. Rev. Lett.* **69**, 1232 (1992).
14. M. Y. Shen and S. L. Zhang, *Phys. Letts. A* **176**, 254 (1993).

15. Y. F. Chen, Y. T. Dai, H. P. Chou, D. C. Chang, C. Y. Chang and P. J. Wang, *Appl. Phys. Lett.* **62**, 2713 (1993).
16. K. Chen, X. Huang, J. Xu and D. Feng, *Appl. Phys. Lett.* **61**, 2069 (1992).
17. L. Brus, *J. Phys. Chem.* **90**, 2555 (1986).
18. A. Garscadden, *Proc. Int. Conf. Phenomena in Ionised Gases, Invited Papers, Pisa (Italy), 8-12 July, 1991, Pg. 147; Eds. V. Pallechi, D. P. Singh and M. Vaselli.*
19. A. Mitchell, R. A. Gottscho, S. J. Pearton and G. R. Scheller, *Appl. Phys. Lett.* **56**, 821 (1990).
20. G. S. Selwyn, J. S. McKillop, K. L. Haller and J. J. Wu, *J. Vac. Sci. Technol.* **A8**, 1726 (1990)

FIGURE CAPTIONS

- Figure 1.** Schematic representation of the deposition system and the in situ photoluminescence measurement set-up.
'Position A': Sample measurement position
'Position B': Sample deposition position (outside the plasma)
- Figure 2.** Normalised photoluminescence spectra of typical samples:
(a)&(b): Particulates collected outside the plasma ('Position B')
(c)Particulates collected on the electrode.
- Figure 3.** A typical in situ photoluminescence spectrum of particulates suspended in the plasma during processing (The spectrum was recorded by subtracting the plasma emission).
- Figure 4.** Micrograph of a typical particulate as measured in a high resolution transmission electron microscope.

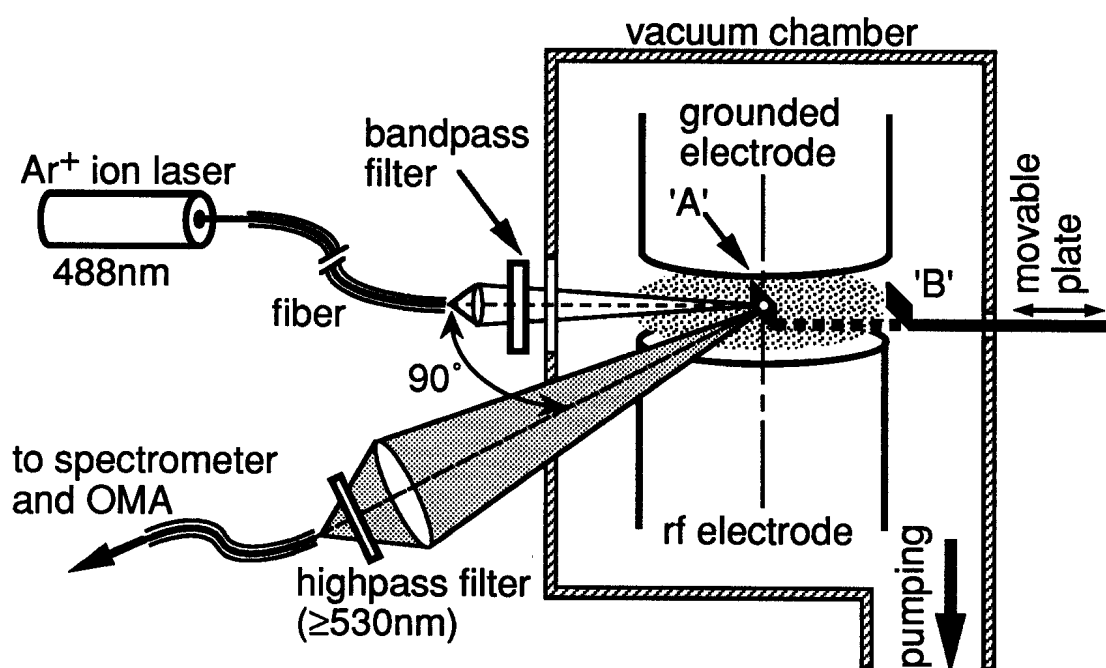


Figure 1.

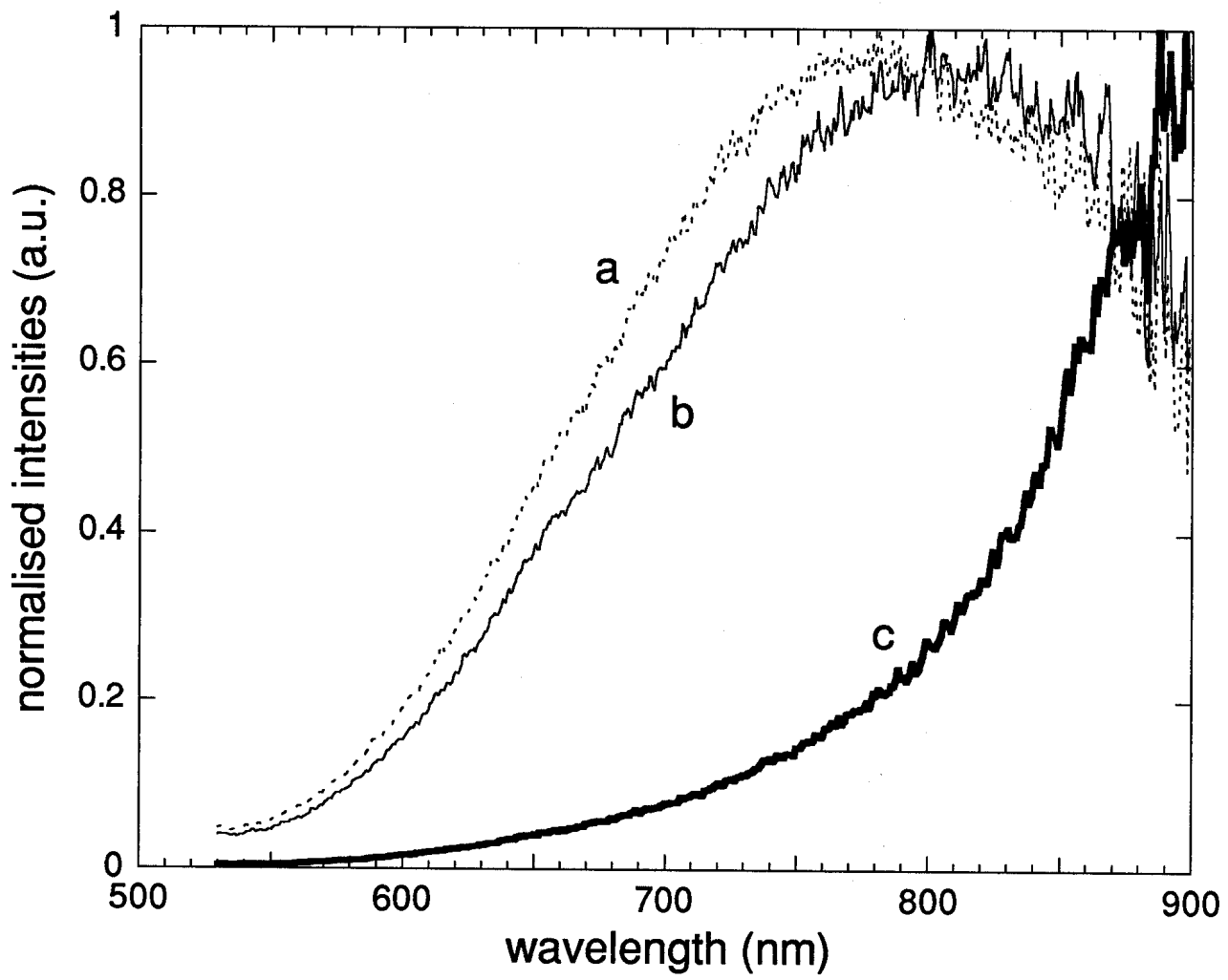


Figure 2

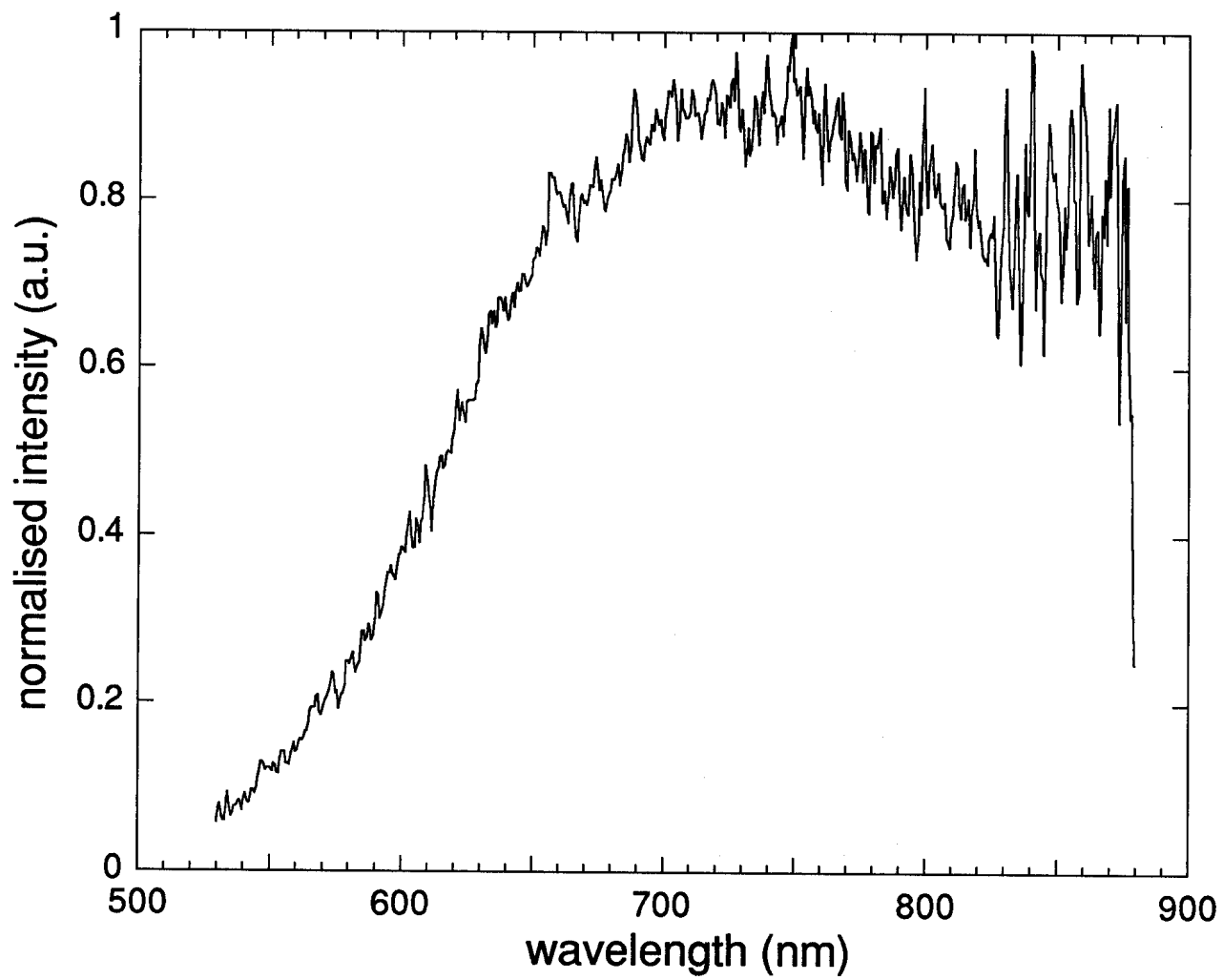


Figure 3.

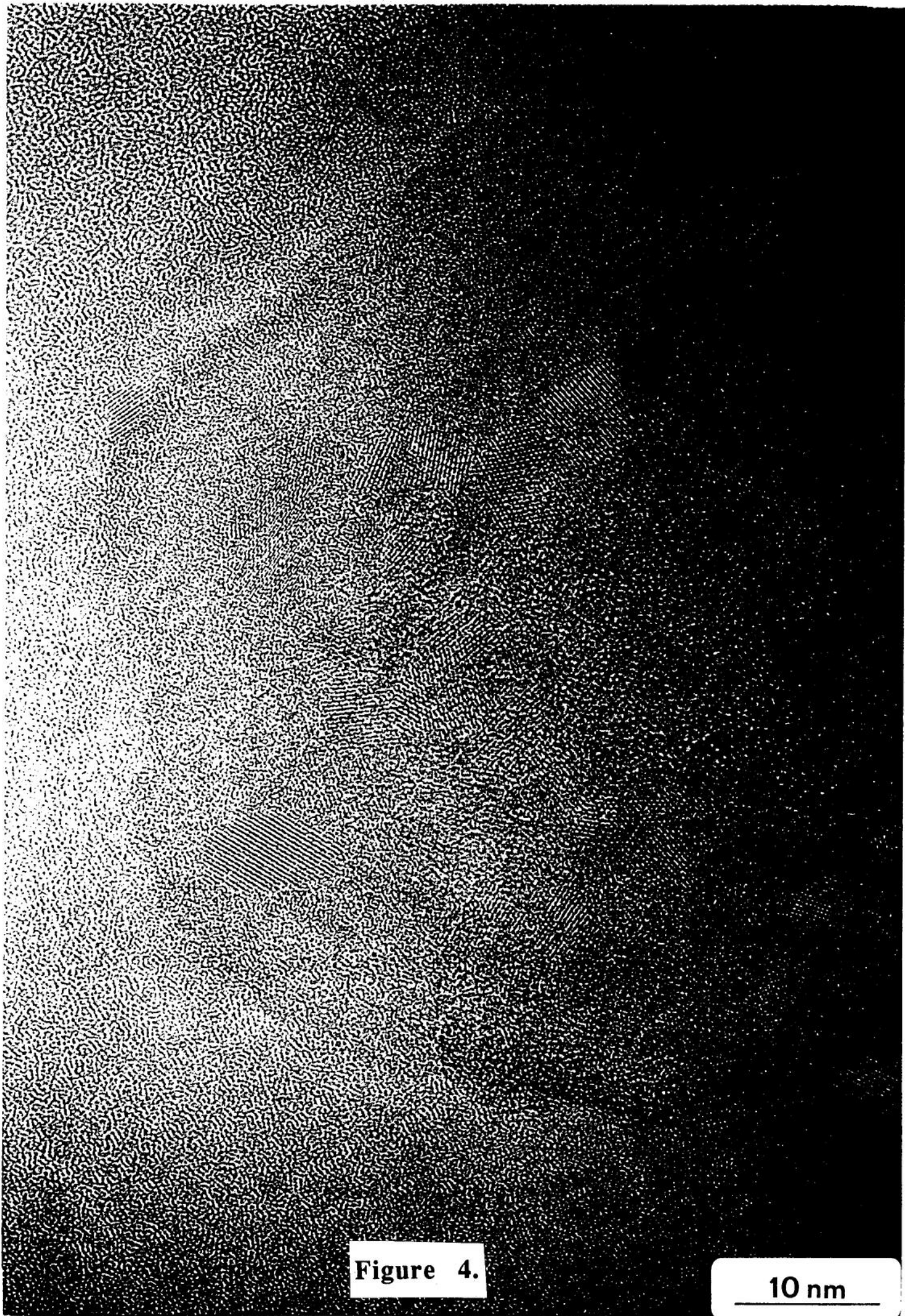


Figure 4.

10 nm