

PROCEEDINGS OF INTERNATIONAL CONFERENCE
NANOMEETING - 2013

**PHYSICS, CHEMISTRY AND
APPLICATIONS OF NANOSTRUCTURES**
REVIEWS AND SHORT NOTES

Minsk, Belarus, 28 - 31 May 2013

editors

V. E. Borisenko

Belarusian State University of Informatics and Radioelectronics, Belarus

S. V. Gaponenko

*B I Stepanov Institute of Physics
National Academy of Sciences of Belarus, Belarus*

V. S. Gurin

Belarusian State University, Belarus

C. H. Kam

Nanyang Technological University, Singapore

 **World Scientific**

NEW JERSEY • LONDON • SINGAPORE • BEIJING • SHANGHAI • HONG KONG • TAIPEI • CHENNAI

Published by

World Scientific Publishing Co. Pte. Ltd.

5 Toh Tuck Link, Singapore 596224

USA office: 27 Warren Street, Suite 401-402, Hackensack, NJ 07601

UK office: 57 Shelton Street, Covent Garden, London WC2H 9HE

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

PHYSICS, CHEMISTRY AND APPLICATION OF NANOSTRUCTURES

Proceedings of International Conference Nanomeeting — 2013

Copyright © 2013 by World Scientific Publishing Co. Pte. Ltd.

All rights reserved. This book, or parts thereof, may not be reproduced in any form or by any means, electronic or mechanical, including photocopying, recording or any information storage and retrieval system now known or to be invented, without written permission from the Publisher.

For photocopying of material in this volume, please pay a copying fee through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA. In this case permission to photocopy is not required from the publisher.

ISBN 978-981-4460-17-0

In-house Editor: Rhaimie Wahap

Printed in Singapore by World Scientific Printers.

FROM NANOVOIDS TO BLISTERS IN HYDROGENATED AMORPHOUS SILICON

C. FRIGERI, L. NASI

CNR-IMEM Institute, Parco Area delle Scienze 37/A, I- 43100 Parma, Italy

M. SERÉNYI, N. Q. KHÁNH

MTA-MFA Institute, Konkoly-Thege ut 29-33, H-1121 Budapest, Hungary

Zs. SZEKRÉNYES, K. KAMARÁS

*Institute for Solid State Physics and Optics, Wigner Research Centre for Physics
Hungarian Academy of Sciences, H-1525 Budapest, Hungary*

A. CSIK

Institute of Nuclear Research of HAS, Bem tér 18/C, H-4001 Debrecen, Hungary

AFM and FTIR spectroscopy were applied to study the relationship between surface blisters and nanovoids in annealed hydrogenated a-Si. The influence of the H bonding configuration on the way the nanovoids give rise to the blisters is discussed. Annealing causes an increase of the polymers density. As they reside on the voids walls their density increase causes an increase of the voids volume. The polymers may release H inside the voids with creation of H₂ gas, whose expansion, upon annealing, further contributes to the volume increase of the voids till the formation of surface blisters.

1. Introduction

Nanovoids are still one of the major defects in hydrogenated amorphous Si (a-Si) [1]. Like in other amorphous materials, nanovoids are usually present in a-Si [2-4]. Since they are empty spaces they bring about density reduction, which can change the refractive index, electronic defect states [1] and inhomogeneous stress distribution if filled with H [5] or if they form Si-H platelets [6]. According to Refs. [7] and [8], voids and related H bonding configurations are also involved in the Staebler-Wronsky effect [9], *i.e.* degradation of the hydrogenated a-Si properties upon illumination. The voids are most crucial if they are large enough to accommodate H molecules [1]. In such a case, in fact, hydrogen may desorb as H₂ with the consequent reconstruction of dangling bonds and Si-Si weak bonds which causes deterioration of the electronic properties [1]. Here we report on the generation of surface blisters from nanovoids in hydrogenated a-Si layers grown by RF sputtering and later annealed. It is argued that the generation is assisted by changes of the H bonding configuration caused by the annealing.

2. Experimental

The 400 nm thick a-Si layers were deposited by RF sputtering on (100) Si substrates in Ar atmosphere at the rate of 6.3 nm/min. Different degrees of hydrogenation were achieved by introducing H into the sputter chamber at the flow rates of 0.4, 0.8 and 1.5 ml/min corresponding to an effective H density of 10.8, 14.7 and 17.6 at.%, respectively, as determined by ERDA (elastic recoil detection analysis). The samples were annealed in high purity (99.999%) Ar at 350 °C for 1 and 4 h. Investigations were performed by atomic force microscopy (AFM) and by Fourier transform infrared (FTIR) spectroscopy by employing a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. FTIR was employed to determine the type of bonding configuration of H to Si by detailed analysis of the stretching mode absorption. The integrated intensity of the absorption peaks contributing to the stretching vibration is used to follow the changes of concentration of the corresponding (SiH) bonds since such intensity is proportional to the absolute concentration apart from a constant [10,11].

3. Results and discussion

Fig. 1 is a typical AFM image of the surface of the hydrogenated a-Si layers after annealing showing the presence of blisters with size of the order of 150-220 nm and height a few nm. Their density and size increase with increasing annealing time and H content.

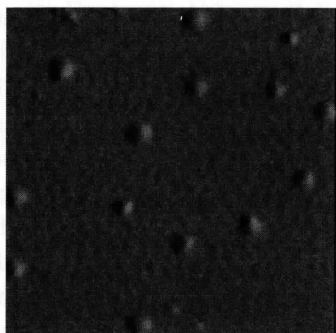


Figure 1. AFM image of surface blisters in the sample hydrogenated at 0.4 ml/min and annealed for 4 h (scan area $5\ \mu\text{m} \times 5\ \mu\text{m}$).

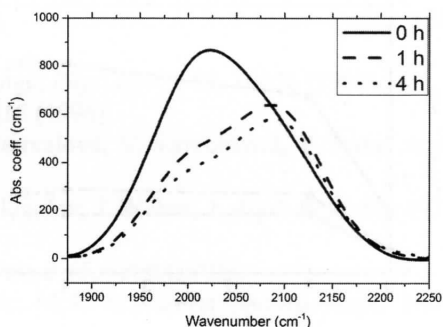


Figure 2. IR absorption spectra in the stretching mode range for the a-Si layer hydrogenated at 1.5 ml/min non-annealed (solid curve) and annealed at 350 °C for 1 h (dash curve) and 4 h (dot curve).

The set of IR spectra of Fig. 2 shows the typical shape of the stretching mode absorption as a function of the annealing time t as observed for all the samples. By gaussian deconvolution applied to the spectra two peaks can be

identified at ~ 2000 and ~ 2100 cm^{-1} , respectively. According to literature, the ~ 2000 cm^{-1} vibration is due to isolated Si-H mono-hydride bonds while the ~ 2100 cm^{-1} one is ascribed to $(\text{Si-H})_n$ clusters and to polymers, such as Si-H₂ dihydrides or chains of them $(\text{Si-H}_2)_n$, $n \geq 2$ [2,10-12]. Upon annealing, the mono-hydride bonds break and their density decreases while the polyhydride density increases and becomes even greater than the monohydride one for H flow rate of 1.5 ml/min. This is summarized in Fig. 3 that gives I_{2100}/I_{2000} as a function of t for the three hydrogenation rates, with I_{2100} and I_{2000} to be the integrated intensity of the absorption peaks at 2100 and 2000 cm^{-1} .

Since the polymers reside on the surfaces of voids [2,10-12], which are usually present in a-Si [2-4], the increased density of the polymers after annealing (Figs. 2 and 3) would thus suggest that the size of the nanovoids has increased to accommodate more polymers with respect to the non-annealed state.

Fig. 2 also shows that the total integrated intensity, *i.e.*, the total H concentration of bonded H of whichever type, decreases with increasing t which indicates that annealing causes the irreversible break of some H bonds to Si. H release from isolated mono-hydrides is expected to be less likely as they represent the deepest binding sites [13]. The polymers decorating the walls of the voids have instead a smaller binding energy [13] and are expected to easily liberate their H into the voids themselves where H atoms may react to form molecular H₂ (Fig. 4).

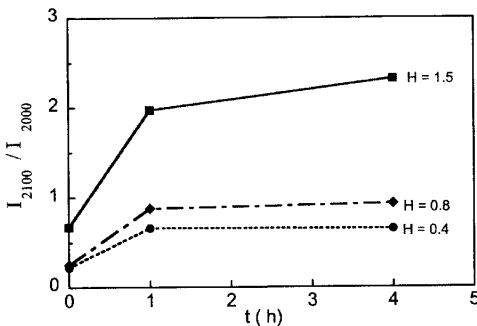


Figure 3. Plot of I_{2100}/I_{2000} as a function of annealing time for the 3 hydrogenation levels.

The molecular H₂ in the gas state inside the nanovoids expands upon annealing with consequent increase of the volume of the nanovoids, which would favour their coalescence leading to bigger and bigger voids. Such bigger voids offer larger inner surfaces for the formation of additional polymers which will further contribute to the release of additional H to be transformed into H₂.

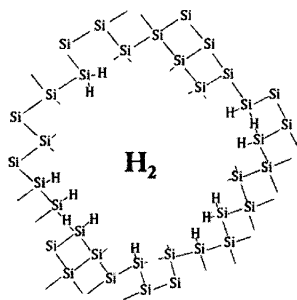


Figure 4. Sketch of the bonding configuration of H to Si in a void. Si-H₂ dihydrides and Si-H monohydrides are assumed to be present. Open short strokes indicate open bonds. It is assumed that some annealing has been applied and that hydrogen has already formed molecular hydrogen, H₂.

Eventually, the voids will reach such a big size to cause a localized lift off of the layers with the formation of surface blisters as observed by AFM. The blisters have thus developed from nanoscopic voids, decorated by (Si-H₂)_n complexes, $n \geq 1$, which have increased their volume because of the increase of the inside pressure due to the thermal expansion of H₂ gas upon annealing.

Acknowledgments

The work has been supported by the Scientific Cooperation Agreement between CNR (Italy) and MTA (Hungary) under the contract MTA 1102 as well as by OTKA grants Nos. K-67969, NF 101329 and CK80126.

References

1. W. Beyer, W. Hilgers, P. Prunici, D. Lennartz, *J. Non-Cryst. Solids* **358**, 2023 (2012).
2. H. Tourir, K. Zellama, J.-F. Morhange, *Phys. Rev. B* **59**, 10076 (1999).
3. S. Acco *et al.*, *Phys. Rev. B* **53**, 4415 (1996).
4. J. Müllerová, L. Prusáková, M. Netrvalová, V. Vavrunková, P. Sutta, *Appl. Surf. Sci.* **256**, 5667 (2010).
5. U. Kroll, J. Meier, A. Shah, S. Mikhailov, J. Weber, *J. Appl. Phys.* **80**, 4971 (1996).
6. W. B. Jackson, C. C. Tsai, *Phys. Rev. B* **45**, 6564 (1992).
7. A. H. M. Smets, W. M. M. Kessels, M. C. M. van de Sanden, *Appl. Phys. Lett.* **82**, 1547 (2003).
8. A. H. Mahan *et al.*, *J. Appl. Phys.* **90**, 5038 (2001).
9. D. L. Staebler, C. R. Wronski, *Appl. Phys. Lett.* **31**, 292 (1977).
10. M. H. Brodsky, M. Cardona, J. J. Cuomo, *Phys. Rev. B* **16**, 3556 (1977).
11. C. Manfredotti *et al.*, *Phys. Rev. B* **50**, 18046 (1994).
12. D. G. Lucovsky, R. J. Nemanich, J. C. Knights, *Phys. Rev. B* **19**, 2064 (1979).
13. W. B. Jackson, C. C. Tsai, *Phys. Rev. B* **45**, 6564 (1992).