ANL/MSD/CP-101088

10509 CONFERENCE PAPER

MEDIUM-RANGE ORDER IN HYDROGENATED AMORPHOUS SILICON MEASURED BY FLUCTUATION MICROSCOPY

RECEIVED
MAY 02 2000
OSTI

P. M. Voyles, Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, IL 61801

H-C. Jin, Department of Materials Science and Engineering and Coordinated Science Laboratory, University of Illinois, Urbana, IL 61801

J. R. Abelson, Department of Materials Science and Engineering and Coordinated Science Laboratory, University of Illinois, Urbana, IL 61801

J. Murray Gibson, Materials Science Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439-4838

M. M. J. Treacy, NEC Research Institute, 4 Independence Way, Princeton, NJ 08540

April 2000

The submitted manuscript has been created by the University of Chicago as Operator of Argonne National Laboratory ("Argonne") under Contract No. W-31-109-ENG-38 with the U.S. Department of Energy. The U.S. Government retains for itself, and others acting on its behalf, a paid-up, nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

Distribution:
1-2. PRS
3. J. M. Gibson
4. L. E. Rehn
5. J. Coble
6. File

Conference Paper to be presented at the 2000 Spring Meeting of the Materials Research Society, San Francisco, CA, April 24-28, 2000.

*Work supported by the U.S. Department of Energy through the Basic Energy Sciences-Materials Sciences under contract No. W-31-109-Eng-38.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

MEDIUM-RANGE ORDER IN HYDROGENATED AMORPHOUS SILICON MEASURED BY FLUCTUATION MICROSCOPY

P. M. VOYLES,[1,2] M. M. J. TREACY,[2] H-C. JIN,[3] J. R. ABELSON,[3] J. M. GIBSON[4], S. GUHA[5], AND R. S. CRANDALL[6]

[1]Dept. of Physics, Univ. of Illinois at Urbana-Champaign, 1110 W. Green St, Urbana, IL 61801
[2]NEC Research Institute, 4 Independence Way, Princeton, NJ 08540
[3]Dept. of Materials Science and Coordinated Science Laboratory, Univ. of Illinois at Urbana-Champaign, 1110 W. Springfield, Urbana, IL 61801
[4]Argonne National Laboratory, 9700 Cass Ave, Argonne, IL 60439
[5]United Solar Systems Corp., 1110 West Maple Road, Troy, MI 48084
[6]National Renewable Energy Laboratory, Golden, CO 80401

ABSTRACT

We have characterized with fluctuation electron microscopy the medium-range order of hydrogenated amorphous silicon thin films deposited by a variety of methods. Films were deposited by reactive magnetron sputtering, hot-wire chemical vapor deposition, and plasma enhanced chemical vapor deposition with and without H_2 dilution of the SiH_4 precursor gas. All of the films show the signature of the paracrystalline structure typical of amorphous Si. There are small variations in the degree of medium-range order with deposition method and H content. The PECVD film grown with high H_2 dilution contains Si crystals ~5 nm in diameter at a density of ~10^9 cm^2. The amorphous matrix surrounding these crystals shows no difference in medium-range order from the standard PECVD film.

INTRODUCTION

Fluctuation electron microscopy is a technique for characterizing medium-range order (MRO) in disordered materials. It has been used previously to demonstrate a reduction in MRO in a-Ge thin films on thermal annealing [1] and in hydrogenated amorphous silicon (a-Si:H) thin films on light soaking [2]. It has also lead to the development of the paracrystalline model for the structure of as-deposited amorphous semiconductor thin films [3].

Fluctuation microscopy works by examining the statistical properties of dark-field electron micrographs acquired at deliberately low image resolution. Electron micrographs of amorphous materials typically show a speckle pattern of bright and dark dots (see Figure 2(a)); the size of each dot is governed by the microscope point-spread function. At low-resolution (~1 nm) one dot represents the scattering from a mesoscopic volume containing ~1000 atoms. A dark-field electron micrograph is an image formed only with radiation that has been diffracted by a particular scattering vector $\boldsymbol{k}$. Put these facts together, and we can qualitatively view a low-resolution dark-field electron micrograph as a position-resolved map of the diffracted intensity from mesoscopic volumes in the sample.

In fluctuation microscopy we compute the normalized variance of the map, defined as

$$V(k,Q) = \frac{\langle I^2(k,Q)\rangle}{\langle I(k,Q)\rangle^2} - 1 \qquad (1)$$

where $\langle\ \rangle$ indicates averaging over the image and k and Q are defined below. This function is

Table I. Deposition parameters for the investigated a-Si:H thin films. T_s is the substrate temperature, r_d is the deposition rate, and t is the thickness.

Sample	T_s (°C)	r_d (Å/s)	t (Å)	Other parameters
RMS < 1 at. % H	230	2.9	210	1.5 mTorr Ar, no H
RMS 15 at. % H	230	2.9	160	1.5 mTorr Ar, 0.8 mTorr H
RMS 20 at % H	230	2.9	140	1.5 mTorr Ar, 2 mTorr H
HWCVD		8.0	320	
PECVD†	200-300		210	50-150 mW/cm^2 RF power, 1 Torr
H-dilution PECVD†	200-300		210	PECVD + ~150:1 H_2:SiH_4

†Details of the deposition are proprietary to United Solar Systems Corporation.

sensitive to large excursions in the image intensity away from the mean. To understand qualitatively how fluctuation microscopy works, consider the variance of the "diffraction map" for two prototypical samples. One is a random collection of atoms, while the other contains randomly oriented ordered clusters of atoms. In the random sample, each mesoscopic volume will be statistically similar in structure and therefore have a similar diffracted intensity. The whole image will be near the mean value and $V(k,Q)$ will be small. In the sample with randomly oriented clusters, some of the clusters will be near a Bragg condition and diffract strongly, leading to bright spots in the image, while others will not be near a Bragg condition and will not diffract strongly, leading to a dark spots in the image. The image overall will have large excursions away from the mean intensity and a large $V(k,Q)$. Thus, $V(k,Q)$ is sensitive to differences in MRO.

Quantitatively, we extract information by varying the imaging conditions and measuring $V(k,Q)$. The scattering vector k controls the diffracting condition of the radiation that makes up the image. The microscope resolution $0.61/Q$ controls the size of the mesoscopic sampling volume. Varying k at constant Q is variable coherence TEM. Varying Q and constant k is variable resolution TEM. We have shown that $V(k,Q)$ gives information about the three- and four-body atomic correlation functions [4] (unlike diffraction, which gives information about the two-body correlation function), and that these higher-order correlations are more sensitive to MRO [5].

This paper deals with variable coherence measurements, given as $V(k)$) for constant image resolution $0.61/Q \cong 1.5$ nm. Information comes from the position and height of peaks in $V(k)$. Peaks are generally found at the positions of diffraction maxima of the underlying material. The height of these peaks indicates the relative MRO of the material.

EXPERIMENT

We have examined six different a-Si:H thin films. The deposition parameters of all the films are summarized in Table I. All of the films were deposited on aluminum foil substrates. Three films were deposited by reactive magnetron sputtering (RMS) from a Si target in an Ar/H_2 atmosphere. The RMS technique allows continuos control of the H content of the resulting film by varying the H partial pressure during deposition [6]. We have examined films with <1 at. % H, 15 at. % H, and 20 at. % H. One film was prepared by hot-wire chemical vapor deposition (HWCVD) in the National Renewable Energies Laboratory (NREL) reactor. Two films were deposited by radio-frequency plasma-enhanced chemical vapor deposition (PECVD) by United Solar Systems Corporation. One of these films was grown with high H_2 dilution of the SiH_4 precursor gas, and the other is standard material. All the CVD films were deposited under

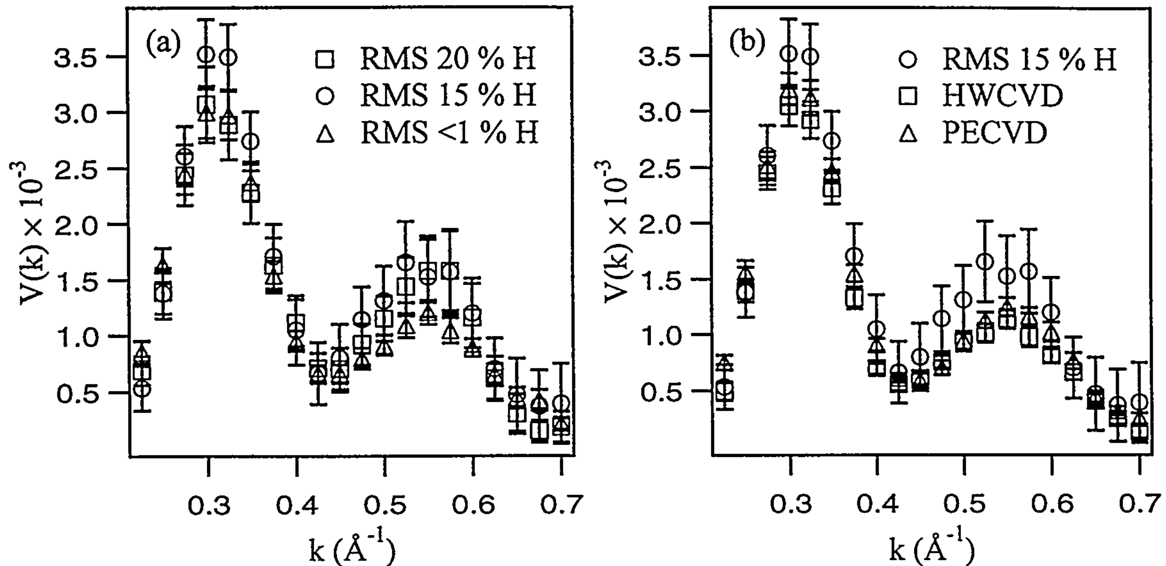

Figure 1. $V(k)$ for (a) the three RMS films with varying H content and (b) the device-quality RMS, HWCVD, and standard PECVD films.

conditions optimized to produce films usable in devices. Film thicknesses were measured in the TEM as described elsewhere [7].

Samples for electron microscopy were created by etching off the Al foil substrate in a 30 % HCL:H_2O solution, then catching the freestanding film on a copper support grid. This sample preparation method creates the large, freestanding areas of film uncontaminated by residual substrate or mounting medium that are necessary for fluctuation microscopy.

Fluctuation microscopy experiments were performed in a Hitachi H9000NAR TEM operating at 200 kV accelerating voltage and an image resolution of ~1.5 nm. The generation of hollow-cone illumination and the acquisition of digital images on a CCD camera have been automated. Each $V(k)$) trace (unless otherwise noted) represents the average of at least ten separate traces with the error bars representing one standard deviation of the mean. The data have been corrected for incoherent image variance and differences in film thickness as described elsewhere [7].

RESULTS AND DISCUSSION

Figure 1 shows $V(k)$ for the RMS films, the HWCVD film, and the standard PECVD film. All of the films show a characteristic double-peak pattern in $V(k)$. The first peak lies at $k = 0.31$ $Å^{-1}$ and the second peak at $k = 0.55$ $Å^{-1}$. These correspond to the first and second diffraction maxima [8] of amorphous silicon [9]. The magnitude of the peaks for all the materials is similar.

This suggests that all of the materials share the same underlying structure, which we have proposed is paracrystalline (PC) [3]. A paracrystal is made up of small strongly strained grains that are topologically crystalline [10] with an amorphous matrix between them. Such a structure has more MRO than a continuous random network (CRN). $V(k)$ calculated from PC molecular dynamics model structures provides a better match for experimental $V(k)$ measurements than $V(k)$ calculated from CRN model structures [3].

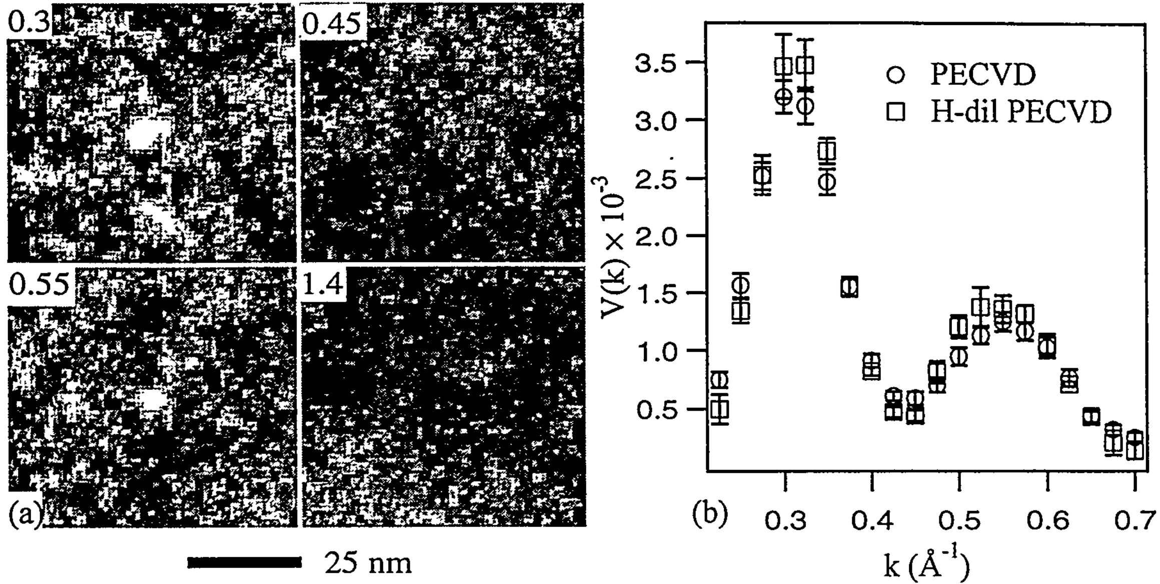

Figure 2. Dark-field micrographs showing the contrast of the ~5 nm crystals in the H-dilution PECVD film at various scattering vectors (indicated in $Å^{-1}$ the upper left corner of each image) and $V(k)$ for the background matrix of the H-dilution film and the standard PECVD film.

There are some very subtle differences in MRO among the films. Figure 1(a) shows the three RMS films with varying H content. The film with 15 at. % H, which has been optimized for use in thin film transistors and other devices, shows slightly more MRO than the films with either higher or lower H content. Figure 1(b) compares the 15 at. % H RMS film, the HWCVD film, and the standard PECVD film. The RMS film shows slightly more MRO, while the HWCVD and the PECVD films the same lower degree of MRO. Too much should not be made of these differences, however, since they are very near the sensitivity of the technique as indicated by the error bars. The error bars are statistical in nature and could be reduced by acquiring additional data, but that would not address possible sources of systematic error, particularly in the incoherent variance contribution and thickness corrections [7].

Figure 2 deals with the high-H dilution PECVD material. As previously noted [11], this material contains small Si crystals. Figure 2(a) shows a series of dark-field micrographs of the H-dilution sample taken at the indicated values of k. The ~5 nm area that appears bright in the $k = 0.3$ $Å^{-1}$ and $k = 0.55$ $Å^{-1}$ images but does not appear above the background in the $k = 0.45$ $Å^{-1}$ or $k = 1.4$ $Å^{-1}$ images is a Si crystal. We estimate that the density of these objects is $\sim 10^9$ cm^{-2}. This estimate is valid only to within an order of magnitude for two reasons. First, the objects are of low enough density and small enough size that it is difficult to achieve good sampling in the TEM. Second, the method we employ will detect only those crystals that are oriented such that one or more of their low-index Bragg reflections is well oriented with respect to the electron beam. It is not possible to calculate what fraction of crystals will or will not be well oriented without making assumptions about the orientation distribution of the crystals. $V(k)$ from areas of the H-dilution film with one or more crystals is completely dominated by the diffraction from the crystal. $V(k)$ in that case with be 5-10 times larger in magnitude, and the relative height of the peaks depends on the orientation of the crystal.

Figure 2(b) shows $V(k)$ for areas of the H-dilution film without crystals compared to the standard PECVD film. Fluctuation microscopy detects no difference in the MRO of the amorphous matrix containing these crystals and the MRO of the bulk of the standard PECVD film. The H dilution trace is the average of only four traces instead of the usual ten due to the difficulty of finding large enough areas of film free of crystals to make the measurements.

CONCLUSIONS

We conclude from the data presented here that a-Si:H films grown by reactive magnetron sputtering (RMS), hot-wire chemical vapor deposition (HWCVD) and plasma-enhanced chemical vapor deposition (PECVD) all share the paracrystalline structure. This makes the paracrystalline structure surprisingly universal, as it is also shared by evaporated a-Ge and a-Si [3] and a-Si formed by self-ion-implantation [12]. We speculate that the paracrystalline structure may be a residual effect of sub-critical crystal nuclei formed during the deposition or implantation process and then frozen in, but significant additional work is necessary to fully develop this hypothesis.

Small differences in the MRO of a-Si:H thin films have been found with changes in H content and deposition method. In the RMS films, the film with the optimum H content for device applications also has the greatest MRO. Across deposition methods, the RMS material has the greatest MRO and the HWCVD material has the least. Of the samples examined, the HWCVD [13] and H-dilution PECVD [14] materials show greater resistance to the increase in resistivity with exposure to light called the Staebler-Wronski effect (SWE) [15], than the RMS material [16]. This lends some credence to our earlier claim [2] that *less* MRO, not more, may be the favorable microstructure for device stability. In the context of the H collision model of the SWE [17], we speculate that perhaps the larger and/or denser PC grains in the RMS material create greater strain and more connected pathways of strained bonds at the grain boundaries which may enhance local H diffusion, leading to more SW defects.

We also conclude that the high H-dilution PECVD material from U.S.S.C. contains crystals ~5 nm in diameter at a concentration of 10^9 cm^{-2} in a matrix which has MRO indistinguishable from that of PECVD a-Si grown without H-dilution. This material is different from other forms of a-Si in several ways, including its behavior under thermal annealing [18], and its optical properties and increased stability against light soaking [14]. It has been proposed that these differences are due to H-induced subsurface reconstruction of the growing film leading to a reduction in strain which enhances the films' MRO [19, 20, 21]. We find no evidence of enhanced MRO in the background matrix of the film. We therefore suggest that the previous observations of enhanced MRO, which used techniques such as x-ray diffraction [21] and spectroscopic ellipsometry [19, 20] that average over macroscopic areas of the film, are measuring the effects of the small concentration of crystals. However this does not necessarily mean that there is no strain reduction in films grown under H-dilution, as it may be possible to have a bond reconstruction which affects short range order and strain only without changing MRO. It also remains to be seen whether or not the optical and stability properties of this material can be explained by the presence of crystals of the size and density reported here and their interfaces with the amorphous matrix.

ACKNOWLEDGMENTS

P.M.V. acknowledges the support of the National Science Foundation (DMR 97-03906). H.C.J. and J.R.A. acknowledge the support of NREL (ADD-9-18668). We thank Peggy Bisher for technical assistance.

REFERENCES

[1] J. M. Gibson and M. M. J. Treacy, Phys. Rev. Lett. **78**, 1074 (1997).

[2] J. M. Gibson, M. M. J. Treacy, P. M. Voyles, H-C. Jin, and J. R. Abelson, Appl. Phys. Lett. **73**, 3093 (1998).
[3] M. M. J. Treacy, J. M. Gibson, and P. J. Keblinski, J. Non-Cryst. Solids **231**, 99 (1998).
[4] J. M. Gibson and M. M. J. Treacy, to be published in Ultramicroscopy.
[5] P. M. Voyles, J. M. Gibson, and M. M. J. Treacy, to be published in J. Electron Microscopy.
[6] M. Pinarbasi, N. Maley, A. Myers, and J. R. Abelson, Thin Solid Films **171**, 217 (1989).
[7] P. M. Voyles, M. M. J. Treacy, J. M. Gibson, H-C. Jin, and J. R. Abelson, in *Advances in Materials Problem Solving with the Electron Microscope*, C. W. Allen, J. Bentley, U. Dahmen, and I. Petrov, eds., Mat. Res. Soc. Symp. Proc. **589**, to be published.
[8] For historic reasons, electron microscopists define $k = 1/\lambda$ instead of $k = 2\pi/\lambda$, so the units here are 2π smaller than those used in x-ray diffraction.
[9] K. Laaziri, S Kycia, S. Roorda, M. Chicoine, J. L. Robertson, J. Wang, and S. C. Moss, Phys. Rev. Lett. **82**, 3460 (1999); Phys. Rev. B **60**, 13520 (1999).
[10] M. M. J. Treacy, P. M. Voyles, and J. M. Gibson, to be published in J. Non-Cryst. Solids.
[11] D. V. Tsu, B. S. Chao, S. R. Ovshinsky, S. Guha, and J. Yang, Appl. Phys. Lett. **71**, 1317 (1997).
[12] J. M. Gibson, J-Y. Cheng, P. M. Voyles, M. M. J. Treacy, and D. C. Jacobson, in *Microstructural Processes in Irradiated Materials,* S. J. Zinkle, G. Lucas, R. Ewing, and J. Williams, eds., Mat Res. Soc. Symp. Proc. **540**, 1999, p. 27.
[13] A. H. Mahan and M. Vanacek, AIP Conf. Proc. **234**, 195 (1991).
[14] S. Guha, K. L. Narasimhan, and S. M. Pietruszko, J. Appl. Phys. **52**, 859 (1981); R. Platz, S. Wagner, C. Hof, A. Shah, S. Weider, and B. Rech, J. Appl. Phys. **84**, 3949 (1998).
[15] D. L. Staebler and C. R. Wronski, Appl. Phys. Lett. **31**, 292 (1977).
[16] Y. H. Liang, N. Maley, and J. R. Abelson, J. Appl. Phys. **75,** 3704 (1994).
[17] H. M. Branz, Sol. State Com. **105**, 387 (1998); Phys. Rev. B **59**, 5498 (1999).
[18] A. H. Mahan, W. Beyer, D. L. Williamson, J. Yang, and S. Guha, to be published in J. Non-Cryst. Solids.
[19] J. Koh, Y. Lee, H. Fujiwara, C. R. Wronski, and R. W. Collins, Appl. Phys. Lett. **73**, 1526 (1998).
[20] J. Koh, H. Fujiwara, R. W. Collins, Y. Lee, and C. R. Wronski, J. Non-Cryst. Solids **227-230**, 73 (1998).
[21] S. Guha, J. Yang, D. L. Williamson, Y. Lubianiker, J. D. Cohen, and A. H. Mahan, Appl. Phys. Lett. **74**, 1860 (1999).