Submicrocrystallites and the Orientational Proximity Effect

A. Ourmazd
AT&T Bell Laboratories, Holmdel, New Jersey 07733

and

J. C. Bean and J. C. Phillips
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
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High-resolution transmission-electron-microscopic lattice images of 10-nm-thick cross sections of 10^3-nm a-Si films deposited at room temperature on clean Si wafers reveal 3-nm clusters, which are orientationally ordered within 80 nm of the substrate-film interface. All previous studies were done in plan view, on films not deposited on clean crystalline substrates, and so did not observe this new effect. Independent evidence suggests that deposition on a clean crystalline substrate generates superior submicrocrystalline morphological order *throughout* the entire 10^3-nm film.

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For more than five decades two models of the structure of noncrystalline network solids have contended for scientific acceptance: the submicrocrystallite[1] and the continuous random network[2] (CRN) models. In Western papers the CRN model has generally been favored,[3] although a few exacting and comprehensive analyses of informative data have supported the submicrocrystallite model.[4,5]

The greatest weakness of the submicrocrystallite model has been the absence of direct observations by high-resolution transmission electron microscopy (HRTEM) of submicrocrystallites of a definite size small enough to give broad Laue diffraction rings[6] and broad Raman-scattering optic-phonon bands.[7] Early HRTEM lattice images in *plan view* of 10-nm-thick films have been thought to be inconclusive,[8] because optical diffractograms of areas 5 nm in diameter showed only Laue rings. Recently *plan-view* lattice images of free-standing, 2-nm-thick Ge films showed 1.4-nm submicrocrystallites,[5] which, presumably as a result of their small size, were not analyzed by optical diffractometry of the lattice images. Samples were prepared and later micrographed in high vacuum, but these elegant experiments still left open the question of whether submicrocrystallites are present in films with more typical thicknesses of 10^2–10^3 nm.

In this Letter we report evidence for 1.5–3-nm submicrocrystallites in a-Si observed by HRTEM lattice imaging in 10-nm-thick *cross sections* of 10^3-nm films of a-Si. The films were deposited at room temperature, in ultrahigh vacuum, on Si wafers which were cleaned by Ar ion sputtering and annealed at 800 °C to remove surface damage. Cross sections were prepared by Ar-ion–beam milling at low power (3 kV, 30 μA), with the samples held at 100 K. Electron micrographs were obtained with a Philips model 420ST TEM, operating at 120 kV. Lattice images were obtained with the electron beam parallel to the substrate ⟨110⟩ direction. The defocus was slightly greater than the Scherzer value, so that information at the (111) planar spacing of Si was efficiently transferred by the microscope.

The bright-field and weak-beam micrographs of 100-nm-thick specimens shown in Fig. 1 reveal columnar structure in the amorphous film and a thin, highly defective surface layer at the amorphous-crystalline interface. A number of submicrocrystallites are circled in the high-resolution micrograph shown in Fig. 2, where bright or dark spots correspond to pairs of atom columns normal to the plane of the cross-sectional

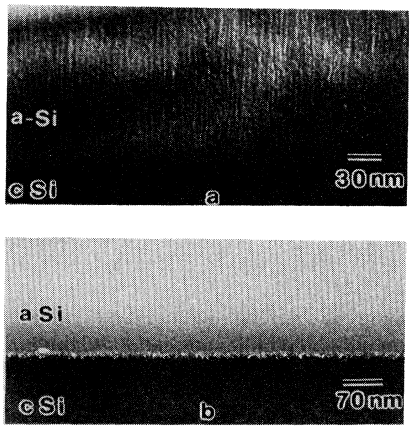

FIG. 1. (a) Bright-field micrograph of a 100-nm-thick specimen showing columnar density oscillations in a-Si on clean c-Si. The oscillations begin about 15–20 nm from the a-c interface. (b) Weak-beam micrograph showing interfacial microcrystalline layer. The width of this layer appears greater in this thick cross section than in the HRTEM picture shown in Fig. 2.

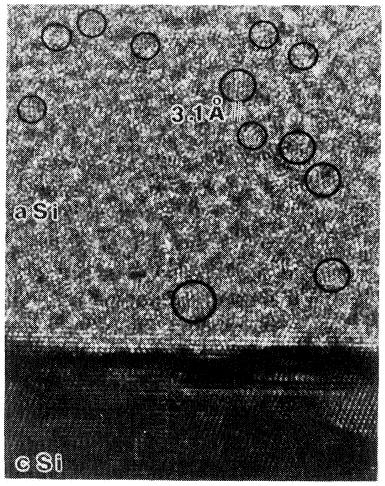

FIG. 2. High-resolution electron micrograph showing many clusters with diameters between 1.5 and 3 nm in a nominally 10-nm-thick cross-sectional sample. Lattice fringes are shown in several cases.

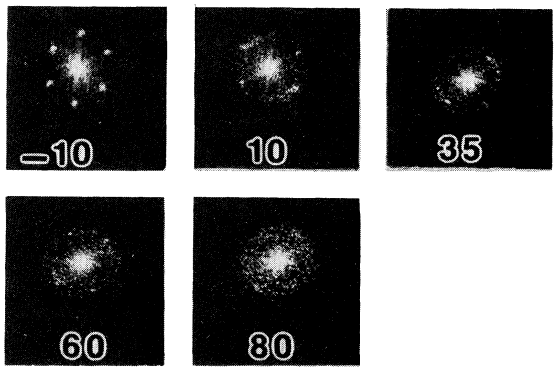

FIG. 3. Optical diffractograms showing the OPE as a function of distance in nanometers from the a-c interface.

sample which has a nominal 10-nm thickness. The observed diameters d of these submicrocrystallites are in the range $1.5\ \text{nm} < d < 3\ \text{nm}$.

While the submicrocrystallites revealed by lattice imaging in Fig. 2 are larger than those previously observed,[5,8] the overall pattern visible to the naked eye remains much the same. The real significance of the present experiments becomes evident only when these lattice images are converted to optical diffractograms based on areas 5 nm in diameter. In place of the Laue rings observed previously,[8] near the interface with the crystalline substrate we now see Bragg spots superimposed on Laue rings (Fig. 3). The orientation of the Bragg spots is nearly parallel to the substrate. With increasing separation from the interface, on a scale of 30–50 nm, the spots fade and lose their parallel registry, while the rings grow in intensity. We term this behavior the orientational proximity effect (OPE).

We believe that the mechanism giving rise to the OPE depends essentially on deposition of the a-Si film on a clean Si substrate in ultrahigh vacuum. In previous plan-view studies the films were deposited either on soluble salt[8] or polymer[5] substrates or on oxidized Si wafers.[9] We suspected that a clean interface would have a dramatic effect on cluster morphology after reviewing[10] a wide range of data, especially from electron spin resonance.[11] These show a fundamental morphological difference between 10^3-nm-thick a-Si films deposited on oxidized compared to clean Si substrates. This bulk effect has been confirmed by luminescence studies of similar films hydrogenated after deposition.[12]

Our provisional model for the OPE assumes that submicrocrystallites with $d \sim 3$ nm dominate the bulk of a-Si 10^3-nm films deposited in ultrahigh vacuum at room temperature on clean Si substrates. Quasiepitaxy with the clean Si + microcrystalline overlayer orients these submicrocrystallites near the interface. The orientational parallel registry relative to the substrate attenuates on a scale of $\lambda \sim 30$–$50\ \text{nm} >> d$, but the submicrocrystallites are still present and remain locally oriented in the film up to thicknesses of order 10^3 nm.

Crystal lattice expansion of hydrogenated microcrystalline Si increases up to 1% with decreasing grain diameter d until $d = d_c$, where $3.0 < d_c < 3.5$ nm, when the 220 and 311 Laue rings collapse into a single ring.[13] Below $d < d_c$ the films were described as "x-ray amorphous." We believe that this collapse occurs when intercluster stress induces plastic intracluster deformations. The OPE produces improved intercluster correlations, reduces intercluster stress without hydrogenation, and increases d for submicrocrystallites up to 3.0 nm. Thus our upper limit for d for nonhydrogenated submicrocrystallites is equal to the lower limit of hydrogenated microcrystalline d defined in diffraction experiments.[13]

There are obvious analogies between the OPE and the ordering of liquid crystals in nematic phases[14] as well as superconductivity induced in thin normal-metal films by superconductive metal substrates.[15] However, there are obvious differences as well, because the size (and possibly the polyhedral morphology) of the submicrocrystallites may be determined self-consistently by the local orientational order. Finally we note that the OPE is perfectly general, and can be used to search for submicrocrystallites in g-SiO_2 on cristobalite,[1,16] for example. It might also be used to confirm the presence of submicrocrystalline clusters in metallic glasses.[17,18]

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[1]J. T. Randall, H. P. Rooksby, and B. S. Cooper, Nature **125**, 458 (1930); K. S. Evstropyev and E. A. Porai-Koshits, J. Non-Cryst. Solids **11**, 170 (1972).

[2]W. H. Zachariasen, J. Am. Chem. Soc. **54**, 3841 (1932).

[3]R. Zallen, *Physics of Amorphous Solids* (Wiley, New York, 1983); S. R. Elliott, *Physics of Amorphous Materials* (Longman, New York, 1983).

[4]J. C. Phillips, Phys. Rev. Lett. **42**, 1151 (1979), and J. Non-Cryst. Solids **43**, 37 (1981); J. E. Griffiths, G. P. Espinosa, J. P. Remeika, and J. C. Phillips, Phys. Rev. B **25**, 1272 (1982).

[5]Y. Saito, J. Phys. Soc. Jpn. **53**, 4230 (1984).

[6]S. C. Moss and J. F. Graczyk, Phys. Rev. Lett. **23**, 1167 (1969).

[7]M. H. Brodsky and M. Cardona, J. Non-Cryst. Solids **31**, 81 (1978).

[8]D. J. Smith, W. M. Stobbs, and W. O. Saxton, Philos. Mag. B **43**, 907 (1981).

[9]A. Chenevas-Paule and A. Bourret, J. Non-Cryst. Solids **59&60**, 223 (1983).

[10]J. C. Phillips, presented at the Materials Research Society meeting, San Francisco, April, 1985 (unpublished).

[11]I. Ohdomari, M. Kakumu, H. Sugahara, M. Hori, and T. Saito, J. Appl. Phys. **52**, 6617 (1981).

[12]B. A. Wilson, unpublished.

[13]S. Vepřek, Z. Iqbal, and F. A. Sarott, Philos. Mag. B **45**, 137 (1982).

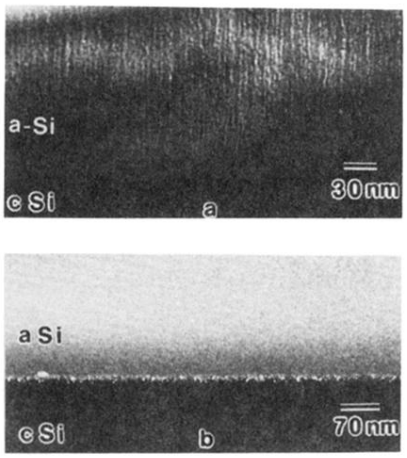
[14]P. G. de Gennes, Mol. Cryst. Liq. Cryst. **12**, 193 (1971).

[15]P. G. de Gennes, Rev. Mod. Phys. **36**, 225 (1964).

[16]J. C. Phillips, Solid State Phys. **37**, 93 (1982).

[17]P. H. Gaskell, J. Non-Cryst. Solids **32**, 207 (1979).

[18]G. Cocco, S. Enzo, M. Sampoli, and L. Schiffini, J. Non-Cryst. Solids **61&62**, 577 (1984).



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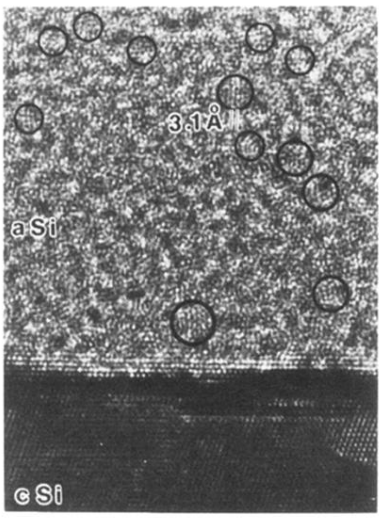

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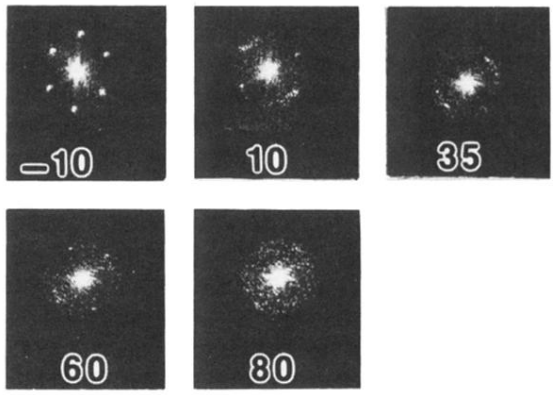

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