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ELASTIC SOFTENING IN NANOCRYSTALLINE SILICON*

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ABSTRACT

It is pointed out that some of the generic physical properties of a nanocrystalline material are similar to those of a grain-boundary superlattice. The structure and elastic properties of a superlattice of twist boundaries on the (110) plane of silicon are calculated as a function of modulation wavelength using a three-body potential. All elastic moduli are found to be softened. This softening is attributed to the relatively small amount of structural disorder at the interfaces.

INTRODUCTION

Nanocrystalline materials are particularly interesting because a large fraction of atoms are at or near an interface, resulting in a great deal of local atomic disorder, and because the absence of bulk material may result in significant changes in the sample dimensions. These two effects are also present in superlattices, which may be considered to be, in some respects, two-dimensional analogs of nanocrystalline materials. If the elastic properties of superlattices on a large number of different crystallographic planes were known, some sort of polycrystalline averaging would allow estimates of the elastic constants and moduli of the nanocrystalline material to be made. Here a first step is made towards such estimate in silicon, by examining the elastic properties of superlattices on one of the principal crystallographic planes.

There has been a great deal of interest in the structural and elastic properties of superlattices since the discovery of anomalous increases in the Young's and biaxial moduli in compositionally modulated structures of Au/Ni and Cu/Pd [1]. Recently, this so-called "supermodulus effect" has also been seen in simulations of grain-boundary superlattices (GBSLs) in metals, in which it was found that, while local atomic disorder at the grain boundary (GB) tends to increase the Young's and biaxial moduli, the decrease in the atomic density at the GB has the opposite effect. Indeed, the hardening due to the local atomic disorder was found to be greater than the softening due to the density decrease, with the overall effect that the Young's and biaxial moduli are

enhanced [2]. By contrast, both the atomic disorder and the dimensional changes were found to decrease the shear moduli.

Here in addition to calculating the elastic properties of GBSLs in silicon, the relative importance of structural disorder and dimensional changes are assessed, thereby illuminating the role of the nature of bonding (metallic vs. covalent).

COMPUTATIONAL METHOD

Because most elastic-property measurements on GBSLs have been performed at low temperatures, all calculations were performed at T=0K. After the equilibrium atomic structure of the GBSL was obtained using a constant-pressure relaxation scheme, the elastic constants and moduli of the system were calculated using a lattice-dynamics like method. The calculated elastic constants are the sum of the well-known Born term and the so-called "relaxation term", the zero-temperature limit of the fluctuation term seen in molecular dynamics. Full details of this method are given in Ref. 4.

The bond-bending and bond-stretching three-body potential of Stillinger and Weber (SW) [5] was used throughout this study. While analytic calculations have shown that the SW potential gives good values for the zero-temperature elastic constants [6], simulations at finite temperature [7] indicate that it also describes the change of elastic constants with temperature, and hence volume expansion, reasonably well. This gives us some confidence that it will be able to correctly describe the elastic behavior in a region of relatively low density around a grain boundary.

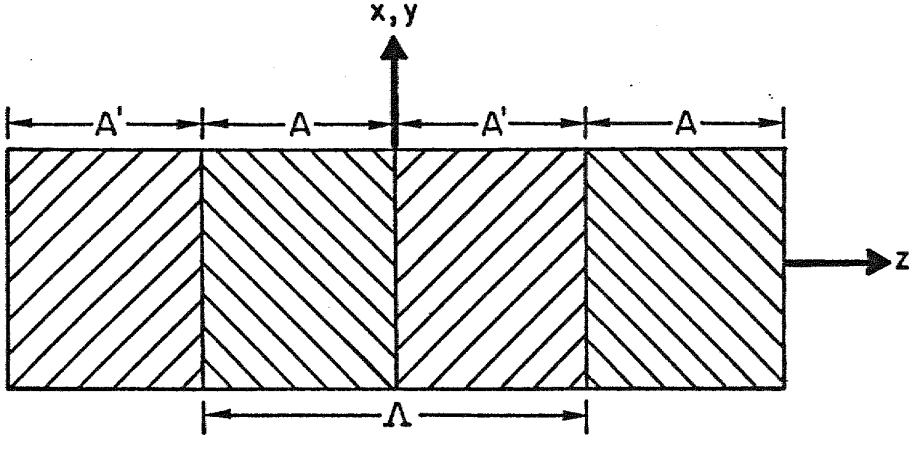

Fig. 1. Periodic arrangement of thin slabs, A and A', to form a "grain-boundary superlattice". A and A' are slabs of the same material which were rotated about the <011> plane normal (II z) to form a periodic array of twist boundaries in the x-y plane.

All calculations were performed on a GBSL on the (110) plane, with twist angle of θ=50.48°. As has been shown previously [8], this so-called Σ11 GB on the second densest lattice plane has properties typical of high-angle twist boundaries.

A schematic of a GBSL is shown in Fig. 1: the z direction is parallel to the GB normal, and the interfaces lie in the x-y plane. The modulation wavelength, Λ, measured in units of the lattice parameter, a, is the distance between every second interface.

STRUCTURE AND ELASTIC PROPERTIES

In a bulk grain boundary, the unit-cell dimensions generally change in the direction of the GB plane normal to accommodate a decrease in atomic density at the interface. By contrast, the unit-cell dimensions in the GB plane are fixed by the far-away perfect-crystal regions in which the GB is embedded, with the result that there are unresolved stresses, similar to a surface tension, at the grain boundary. In a superlattice or a nanocrystalline material there is no far-away perfect crystal, and these stresses may be relaxed by changes in the sample dimensions in the GB plane, the Poisson effect.

Figure 2 shows the average lattice parameters and sample volume of the previously described superlattices as a function of Λ. We note that there is a significant increase in the sample volume, V, which is mainly attributable to an increase in the average lattice parameter in the direction of the GB-plane normal, $\bar{a}_z$. By contrast, $\bar{a}_y$ is only slightly larger than the ideal crystal lattice parameter while $\bar{a}_x$ is only slightly smaller. (This asymmetry in x and y is a reflection of the two principal axes in the GB plane being different: <110> and <100>.)

Figure 3(a) shows the three Young's moduli of the GBSL as a function of Λ. Unlike the hardening observed in the metallic GBSLs [2], they are significantly softened, decreasing to about 60% of their bulk values for the smallest Λ considered. Figure 3(b) shows that the decreases in the the shear moduli are of a similar size, in contrast to the metals where the shear constants were reduced to less than 10% of their bulk values. A GBSL on the (111) plane showed a similar amount of softening in both the Young's and shear moduli as that of the GBSL on the (110) plane [3].

ROLE OF STRUCTURAL DISORDER AND DIMENSIONAL CHANGES

Silicon, like most materials, expands and becomes elastic softer as it is heated. It may be anticipated, therefore, that the increase in system volume shown in Fig. 2 will tend to decrease the elastic strength of the

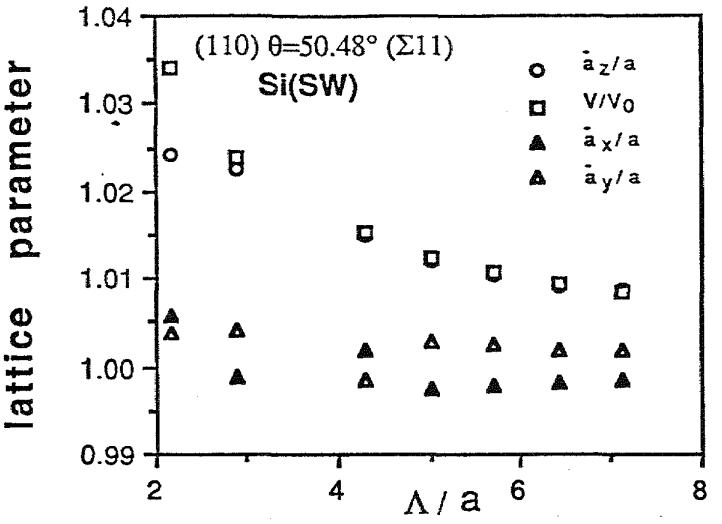

Fig. 2. Relative change in the average lattice parameters, $\bar{a}_x$, $\bar{a}_y$, $\bar{a}_z$, and sample volume, V, as a function of Λ, scaled to their $\Lambda \to \infty$ values.

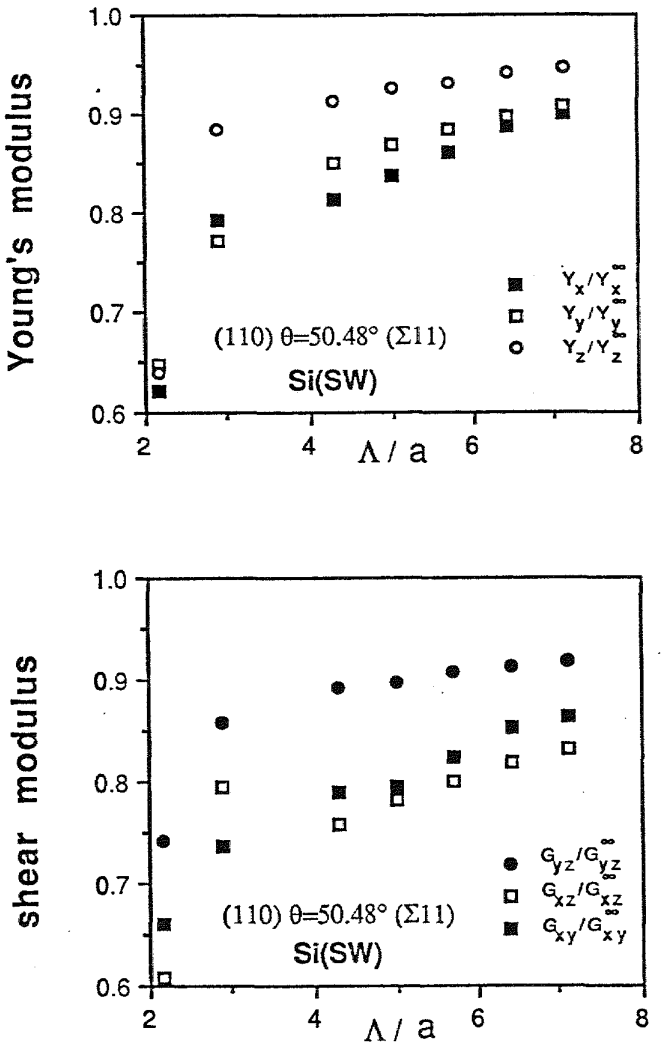

Fig. 3. Variation of (a) the Young's moduli, Y_x, Y_y and Y_z and (b) the shear moduli G_{yz}, G_{xz}, G_{xy} as a function of Λ, relative to their $\Lambda \to \infty$ values.

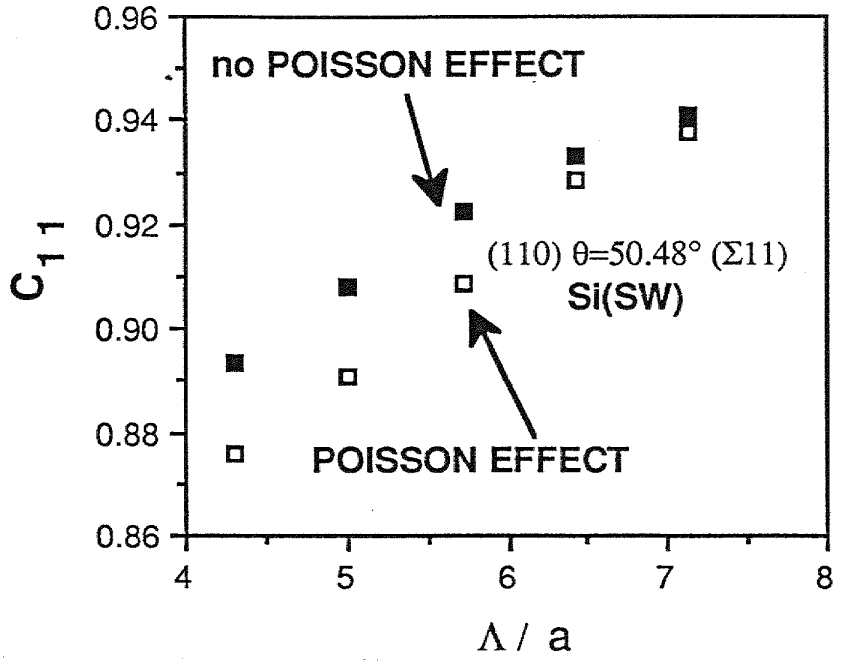

Fig. 4. Variation of C_{11} as a function of Λ, scaled to its $\Lambda \rightarrow \infty$ value, both with and without the Poisson effect.

material. The effect of even small changes in sample dimensions may be strikingly shown by comparing the elastic behavior of superlattices in which the Poisson effect is allowed, with superlattices in which the Poisson effect is suppressed. When the Poisson effect is suppressed the sample expansion is only slightly smaller (by less than 0.02%), but as seen if Fig. 4, the associated difference in C_{11} may be as large as 2%.

The studies in metals showed that pairs of atoms in closer proximity than in the ideal crystal tend to increase some of the elastic moduli of the material. In contrast, pairs of atoms that are further apart than in the ideal crystal tend to decrease the overall elastic strength. In metallic GBSLs the former effect is significantly larger than the latter, with the consequence that structural disorder tends to lead to a significant increase in the elastic strength. On the other hand, as can be seen from an examination of the radial distribution function [3], in silicon superlattices few atoms are closer than their ideal-crystal distances, with the consequence that the structural disorder has little tendency to increase the elastic strength of the material.

Thus the overall effect of the relatively large dimensional changes and only small amount of structural disorder in the silicon GBSLs is that the elastic moduli, and most elastic constants, are significantly decreased.

DISCUSSION AND CONCLUSIONS

In conclusion, in a superlattice of (110) grain boundaries in silicon, all elastic moduli are softened, unlike in metals where strong enhancements of the Young's and biaxial moduli have been observed [2]. This softening may be attributed to the relatively small amount of structural disorder at the interfaces, presumably a consequence of the short range of the potential and the strong three-body interaction.

While a full calculation of the elastic properties of a nanocrystalline material are not currently possible, based on the above results and those for a (111) grain boundary superlattice [3], it may be supposed that there will be no elastic hardening in nanocrystalline silicon.

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