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Pressure Induced Pseudomelting Implied By Negative Clapeyron Slope for Silicon

Md. Naushad Alam*, Aparajita

Author's Affiliations:	
Md. Naushad alam	Department of Physics, G.D. College, Begusarai – 851101, Bihar, India E-mail : nalam884@gmail.com
Aparajita	Department of Physics, B.N. College Patna, Patna University, Patna 800004, Bihar, India. E-mail : nenaaprajitakishore@gmail.com
***Corresponding author:**	**Md. Naushad alam** Department of Physics, G.D. College, Begusarai – 851101, Bihar, India E-mail: nalam884@gmail.com

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ABSTRACT We have studied pressure induced pseudomelting implied by the negative clapeyron slope for Silicon. Pressure induced amorphization was based primarily on Raman measurements. This does not rule out the possibility of a transformation to a phase which may not have a Raman-active mode such as the primitive hexagonal. Energy dispersive x-ray diffraction measurements on the sample had shown pressure induced annealing of nanocrystalline regions. Since this would have resulted in an increase of the particle size and reduced surface effects, the high pressure behavior should have been similar to that of surface terminated nanoparticles. We have observed that the cubic nano π-silicon undergoes a crystalline-crystalline phase transition to the primitive hexagonal phase under high pressure at ~20Gpa and the amorphous phase arised only on release of pressure. This observation is consistent with the transformation seen earlier in the case of surface terminated nanocrystalline silicon. Nanoamorphous phase thus obtained transforms reversibly to the Ph phase under further pressure cycles. The role of particle size in this reversible behavior. Our results showed that the reversible inter conversion also takes place in bulk amorphous Silicon, provided the pressure release is fast, unlike in the case of nanoamorphous Silicon. Our studies showed that irrespective of the method of preparation or size of the amorphous Silicon particles, it always transforms to primitive hexagonal phase under compression. The obtained results were found in good agreement with previously obtained results.

KEYWORDS Pressure, induced, pseudomelting, clapyron slope, amorphourization, transformation, primitive nanocrystalline, surface effect, nanoparticle.

INTRODUCTION

Deb et al. [1] made experimental studies on nanocrystalline porous Silicon, suggested that the initial cubic phase transforms to high density amorphous phase at ~14Gpa, which on release of pressure, converted to a low density amorphous structure. These observations were supported by theoretical calculations of Durandurdu et al. [2] and Martonak et al. [3], the role of pressure on phase transitions in π-Silicon. Silicon is one of the most widely investigated materials, even in the context of structural changes under different thermo dynamical conditions, its behavior has been extensively studied. Mc Millon et al. [4] and Poswal et al. [5] studied that under pressure its structures have been shown to evolve to dense and more highly co-ordinated forms. Tolbert et al. [6] studied that the cubic dimond phase of nanocrystalline Silicon ~50 nm transforms directly to the primitive hexagonal form at 22 Gpa, by passing the β-tin and Imma phases observed in bulk Silicon. Focher et al. [7] studied that in molecular dynamics simulations for bulk silicon, the cubic diamonal phase has been shown to transform to the Ph phase on abrupt pressure increased. Imai et al. [8] presented that β-tin phase becomes inaccessible when silicon is compressed at low temperatures. Domnich et al. [9] and Daisen Berger et al. [10] studied pressure induced crystallization in amorphous silicon.

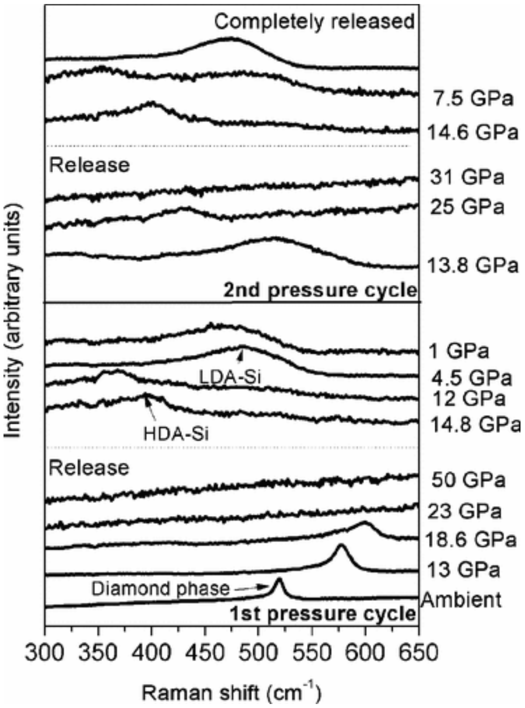
METHOD

The average particle size of the dimond structured nanocrystallites of silicon embedded in porous silicon was determined by a phenomenological three dimensional phonon confinement model. For bulk amorphous silicon, 99.9 % pure amorphous silicon samples were obtained and were characterized by Fourier-transform infrared and Raman spectroscopy.

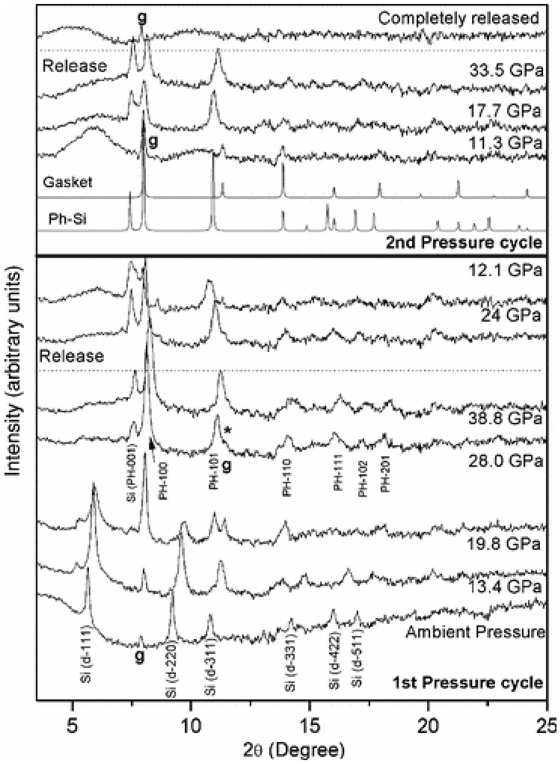
The structure factor of amorphous silicon at ambient conditions was found to be consistent with tetrahedral co-ordination. For high pressure the sample was loaded in a ~150μm hole, drilled in a preindented tungsten gasket of a diamond-anvil cell. Methanol ethanol mixture was used as a pressure transmitting medium and pressure was estimated using the ruby fluorescence method. A few particles of gold were also loaded in the diamond anvil cell to determine the pressure in the cell. For Raman measurements an indigenous confocal optics and suprernotch filter based micro Raman system was used. A solid state pumped laser of wavelength 532nm was used as an excitation source.

RESULTS AND DISCUSSION

Graph (1) shows that on increase of pressure results confirmed the vanishing of the Raman active peak of the cubic phase of π-Silicon beyond 18Gpa. At 23Gpa essentially a flat back ground was observed. Graph (2) shows that π-Silicon does not become amorphous at least upto ~39Gpa. At this pressure the most intense [100] and [101] diffraction peaks of the Ph-phase are visible. The coexistence of the diamond as well as the ph phase of π-silicon is attributed to the first order of the phase transition. It also shows the inhomogeneous distribution of local stresses in the sample. In static high pressure on bulk silicon under ambient temperature, the β-tin phase is realized because there is sufficient relaxation time and thermal energy to overcome the barrier. In the case of nanoparticles because of the absence of intrinsic defects and the substantial energy contribution due to surface modification, high barrier paths become inaccessible. The results do not show the presence of high density amorphous phase on subjecting the cubic diamond phase of porous silicon to higher pressures. We have observed that the Ph. Phase transformed to the high density amorphous phase on release of pressure. The broad band centered at 392cm^{-1} at ~15 Gpa can be assigned to the high density Amorphous phase. On further release of pressure the low density amorphous phase was identified at ~4.5 Gpa, characterized by abroad hump of tetrahedral silicon-silicon stretching vibrations at 484cm^{-1}. Graph (1) also shows that even in the second pressure cycle the low density Amorphous Ph and reverse transformation proceed through a high density amorphous phase. When pressure was released in the second pressure cycle, coexistence of the local density amorphous and high density amorphous phases was observed at ~7.5 Gpa. The low density amorphous phase obtained on release of pressure remains stable over a prolonged period of time, suggesting that this amorphous phase is either a Kinetically preferred state or an energetically preferred state in the case of nano particles.



Graph 1: Raman spectra of π-Si at different pressures.



Graph 2: The pattern at ambient pressure shows all the diffraction peaks of the cubic diamond phase of Silicon.

CONCLUSION

We have calculated the diffraction patterns of both Ph and β-tin phases of Silicon and compared the different ratio of crystalline nucleus diameter d values with those of the observed diffraction patterns. The d values of the Ph phase are closer to the experimentally observed values. So the ph phase is more appropriate representation for the high pressure phase. The amorphous phase when subjected to high pressures transforms reversibly to a higher coordinated primitive hexagonal phase showing a kind of memory effect. The bulk amorphous phase exhibits significant deviation during the decomposition process, is the pressure is reduced slowly it follows the same sequence of transformations as the bulk crystalline silicon. If decompressed fast enough <~60 s we get the local density amorphous phase. Crystallization takes place at a lower pressure of ~15Gpa. The crystallization of an amorphous phase is known to a nucleation and growth process which involves formation of a low density interface layer between the crystalline nucleus and amorphous matrix. The net volume change due to nucleation depends on the size of the nucleus and molar volumes of crystalline and amorphous phases and the interface layer.

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