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Evidence of New High-Pressure Silicon Phases in Fs-Laser Induced Confined Microexplosion

Ludovic Rapp[1], Bianca Haberl[2], Jodie E. Bradby[2], Eugene G. Gamaly[1], Jim S. Williams[2], Saulius Juodkazis[3], Andrei V. Rode[1]
[1]Laser Physics Centre and [2]Electronic Materials Engineering,
Research School of Physics and Engineering, The Australian National University, Canberra ACT 0200 Australia
[3]Swinburne University of Technology, Hawthorn, VIC, 3122, Australia
Author e-mail address: avr111@physics.anu.edu.au

Abstract: We report on formation of high-pressure polymorphs of Si in confined microexplosion experiments. The results show that Si has undergone pressure-induced transitions into the realm of the metallic phases conventionally formed above 11 GPa.

OCIS codes: 260.7120 Ultrafast phenomena; 140.3440 Laser-induced breakdown; 320.7130 Ultrafast processes in condensed matter

1. Introduction: Confined microexplosion

The search for new alternative ways to form novel super-hard materials which benefit mankind is fuelled by recent advances in the notably difficult experimental techniques. Confined microexplosion induced by ultrashort laser pulses focused in the bulk of transparent dielectric to the intensities ~10^{15} W/cm^2, well above the optical breakdown threshold, is a unique method which offers creating simultaneously terapascal pressures and temperatures above 10^5 K in table-top experiments. The extreme conditions of the ultrafast microexplosion exist only in a small volume at the focal region, allowing the creation of these conditions with micrometer-scale precision. Fs-laser pulses can deposit a volume energy density up to several MJ/cm^3 in a sub-micron volume. This creates highly non-equilibrium, hot, dense and short-lived plasmas with conditions favorable for arrangement of atoms into unusual material phases. The accompanied record-high heating ~10^{17} K/s and quenching ~10^{14} K/s rates keep the transformed material 'frozen' inside the pristine structure [1-7]. So-called Warm Dense Matter (WDM) and novel non-equilibrium processes such as formation bcc-Al by microexplosion in sapphire and preserved in amorphous Al_2O_3 matrix have recently been produced by this method [1,2].

While the femtosecond-microexplosion demonstrated the potential to create entirely new material states, the method is widely considered as suitable only for transparent dielectrics [1-7]. Here we expand the confined microexplosion method into the domain of non-transparent materials such as Silicon. We have chosen to study high-pressure phases of Si for the following obvious reasons. The metastable high-pressure phases of silicon have attracted much attention since they can be easily integrated into existing Si technologies in which their alternative properties can be utilized. Indeed, Silicon has a large impact on the world economy and modern technology. So far, twelve different high-pressure crystalline phases revealed in a pressure range up to 250 GPa, which is close to the upper limit of pressure achievable by the diamond anvil cell. A major goal of our studies is to find new structural phases of Si formed in highly non-equilibrium conditions of confined microexplosion.

2. Experimental

In our experiments ~0.1-1.0 μJ, 170-fs laser pulses were focussed with a ×150 microscope objective (NA=1.45) on a Si surface buried under 10-μm thick SiO_2-layer of the oxidised Si wafer to form the conditions of confinement. We have chosen the thickness of the SiO_2 layer to be 10 μm, which is not so deep for developing large spherical aberrations with high-NA focusing optics and at the same time guarantee the absence of optical breakdown at the surface. The thickness of the boundary between the transparent oxidised layer and crystalline Si where the laser radiation is focused is of the order of only 2 nm, it can be clearly seen in electron microscope. The laser pulses were tightly focused to the intensity 10^{15} W/cm^2, well above the threshold ~10^{12} W/cm^2 for optical breakdown and plasma formation. The experiments were conducted with laser pulses at 1 kHz repetition rate in a moved at a rate 2 mm/s to guarantee a single shot per spot regime, so that each of the shot was located 2 μm apart. Samples of the shock-wave modified regions were opened using focused-ion beam milling, and analysed with scanning and transmission electron microscopy and Raman microspectroscopy.

3. Results

TEM analysis of the laser-modified zone showed that a void was formed surrounded by a shock-wave-modified Si. The material surrounding the void was found to contain a number of different phases including amorphous Si and several new silicon polymorphs with inter-atomic spacing that cannot be attributed to any known polymorph of silicon. Indeed, electron dark-field imaging clearly shows that several phases form fully within the silicon matrix.

At least twelve Si polymorphs with different electronic and optical properties are known to exist at pressures up to 250 GPa [9]. In our samples we observe new silicon polymorphs with inter-atomic spacing of 4.38 Å, 2.41 Å, and 2.15Å, as determined from transmission electron diffraction patterns of shock-wave compressed silicon. These inter-atomic spacings cannot be attributed to any known polymorph of silicon. In addition, pressure-induced twinning of the silicon lattice, similar to that in germanium [8], was obtained for the first time. The new phases coexist with the known high-pressure hexagonal-diamond (hd, Si-IV), traces of tetragonal (Si-VIII) and rhombohedral (r8, Si-XII) phases [9], as well as conventional diamond-cubic silicon crystal (dc, Si-I).

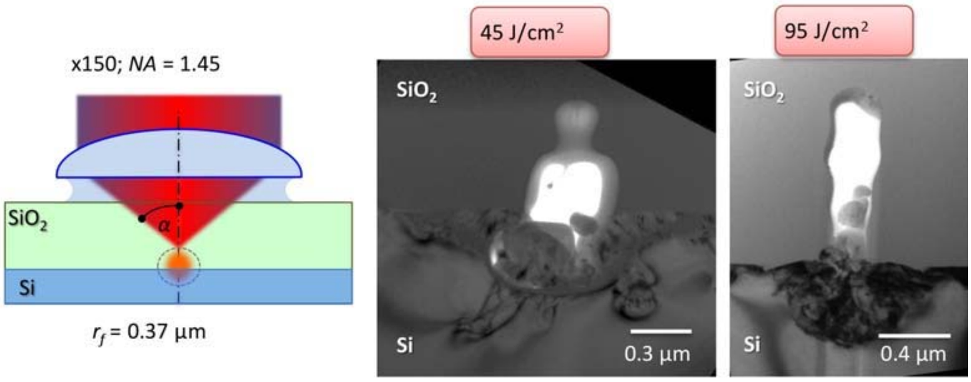

Fig. 1. Focusing arrangement of laser energy on the surface of Si buried under a SiO_2 layer and TEM-images of voids in SiO_2 (white area) and compressed Si (dark areas under the voids) where the new high-pressure Si polymorphs were observed.

The formation of these new polymorphs is evidence that Si has undergone pressure-induced transitions into the realm of the metallic high-pressure phases that are conventionally formed above 11 GPa [10]. These phases may provide a means for localized band-gap engineering at the nanoscale, in a similar manner to the potential of Si-XII for photovoltaic applications [11]. Reliably repeatable in many experiments, evidence of the formation of structures currently not assigned to any known phases of silicon were detected.

The ability of ultrafast lasers to locally modify the electronic properties of silicon with sub-micron precision with repetition rates up to and above 10^5 shots per second in a simple bench-top experiment, opens up novel opportunities for nanoelectronics through the incorporation of such nanostructures into semiconductor devices.

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5. References

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