Optical and Electronic Properties of Nanoscale Si/SiO_2 Superlattices

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This invited talk is focused on the fabrication and characterization of layered Si-based nanostructures, which have been called nanocrystalline silicon (nc-Si)/silicon dioxide superlattices [1]. Among the many semi-conducting materials, silicon is one of the most studied and definitely the most important material for commercial microelectronics. During the last several decades, the exponential growth of electronic chip complexity and drastic decrease of transistor dimensions has highlighted new directions in electronic device evolution and the potential applicability of Si nanocrystals for nanoelectronics and integrated light-emitters. The latter was stimulated by the discovery of efficient light emission in different forms of Si nanostructures [2] and by the demonstration of a Si-based light-emitting device prototype integrated into conventional microelectronic circuitry [3]. Hence, the interest in reliable fabrication of Si based nanostructures with control over the nanocrystal size, shape, and crystallographic orientation has been growing continuously over the last decade. Recently, the application of Si nanocrystals in electronic devices was suggested and proved by the demonstration of a Si nanocrystal non-volatile memory and other devices utilizing the Coulomb blockade effect [4, 5].

Despite the strong interest in different forms of nc-Si, the fabrication of Si nanocrystals with control over the nanocrystal size and shape was significantly less successful compared to other semiconducting materials. The latest progress in semiconductor nanocrystal fabrication has been based on advances in chemical synthesis in II-VI materials [6] and the successful application of the Stranski-Krastanow growth mode in molecular beam epitaxy (MBE) for III-V semiconductors. Neither of these techniques is applicable for Si/SiO_2 structures. In general, crystalline Si (c-Si) and amorphous SiO_2 are quite different materials with large mismatches between local crystallographic order and thermal expansion. Therefore, crystalline Si does not wet the SiO_2 surface, and standard heteroepitaxy based on MBE, chemical vapor deposition (CVD) or magnetron sputtering, produces highly disordered polycrystalline Si on SiO_2-covered substrates. Several attempts to introduce layered Si/SiO_2 nanoscale structures were reported in the mid and late 1990s, aiming for deep carrier confinement in Si nanocrystals due to the high SiO_2 barriers. Two major approaches were focused on (1) high quality amorphous Si (a-Si)/amorphous SiO_2 (a-SiO_2) structures [8] and (2) layers of Si nanocrystals sandwiched between tunnel transparent, nanometer-thin a-SiO_2 separating layers [1]. In the former case, involving a-Si layer thicknesses between 1 and 2 nm, the ultrathin Si layers could not be crystallized even after extended annealing at high temperatures owing to the strain at the Si/SiO_2 interface [9]. Nevertheless, clear optical evidence of carrier confinement in the Si layers was obtained [9, 10]. The other approach utilizes a unique property of the c-Si/SiO_2 interface, the same property that made the MOSFET the unique generic device for modern electronics. Since crystalline (or nanocrystalline) Si and amorphous SiO_2 belong to different thermodynamic classes of materials, they do not mix but rather segregate at high temperatures. Therefore, an atomically smooth interface and very homogenous growth of SiO_2 on c-Si can be produced by a simple technological procedure: Si thermal oxidation. In general, controlled crystallization of amorphous Si/SiO_2 superlattices follows the same rules with only one exception: the a-Si layer must be crystallized before interstitial oxygen diffuses into the Si layer. It was realized almost immediately that rapid thermal annealing, which currently is a standard fabrication procedure for many semiconductor processes, is able to provide very fast crystallization of nanometer thick a-Si layers. At the same time, an a-SiO_2 layer remains amorphous, because annealing at temperatures close to 1200^oC merely improves its stoichiometry.

This technological process is able to produce layers of Si nanocrystals sandwiched between a-SiO_2 layers or nc-Si/a-SiO_2 superlattices. In view of considerable prior research, the physical properties of these structures could be expected to be similar to that of grainy polycrystalline Si and should be affected by nanocrystal (or nanograin) boundaries. However, it turns out that many interesting and unique properties of nc-Si/a-SiO_2 superlattices stem from their vertical periodicity and nearly defect-free, atomically flat, and chemically abrupt nc-Si/SiO_2 interfaces [11]. In addition, by combining a less than 5% variation in a-Si layer thickness with control over the Si nanocrystal shape and crystallographic orientation [11], a system of nearly identical Si nanocrystals can be produced and studied.

The aim of this talk is to review in detail the fabrication of nc-Si/a-SiO_2 superlattices and their structural and optical (mainly Raman scattering and photoluminescence) properties. Recently, a number of surprising results such as resonant tunneling and quantum carrier transport [12] were obtained from investigations of the electronic properties of these structures. Carrier transport in layered structures of Si nanocrystals is a complex subject, and by itself could provide material for another talk. Therefore, we only briefly mention here the most interesting and significant results on the electronic properties of nc-Si/a-SiO_2 superlattices.

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