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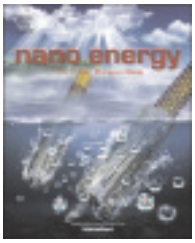

RAPID COMMUNICATION

Efficient thermoelectric performance in silicon nano-films by vacancy-engineering

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Abstract
The introduction of large concentrations of lattice vacancies in silicon nano-films creates more than a 20-fold reduction in thermal conductivity, while electrical conductivity and Seebeck coefficient are largely maintained. This results in thermoelectric performance comparable to silicon nanowires, but crucially leaves the silicon structure indistinguishable from bulk silicon, resulting in a robust material that is straight-forward to fabricate. This finding significantly advances the potential of silicon ultra-thin-films as a high-performance thermoelectric material.

Introduction

Silicon (Si) is a remarkably useful element. Its abundance, low cost and low toxicity, combined with vast practical know-how means it is a leading material on which to base technologies. However for good reason, certain applications have under-utilised Si, with thermoelectrics (TE) being one example. Three material characteristics determine TE performance – thermal conductivity (κ), Seebeck coefficient (S) and electrical resistivity (ρ). These interlinked properties are often combined along with absolute temperature (T) to describe performance in terms of the dimensionless figure-of-merit (ZT), where $ZT=S^2T/\rho\kappa$. Compared to other materials, highly-doped Si (doping $\sim 10^{19}$-10^{20} cm^{-3}) has desirably large S and small ρ, but these are negated by high thermal conductivity, meaning that ZT is relatively poor for bulk Si ($ZT\sim 0.01$ at 300 K [1]), about 100-fold worse than for popular TE materials such as bismuth telluride (Bi_2Te_3) ($ZT\sim 1$).

Nanowires

Only in the past few years has it been demonstrated possible to vastly reduce Si's thermal conductivity with little or no effect on S or ρ [2,3]. In structures such as Si nanowires

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(SiNWs), the long-wavelength phonon modes, which strongly contribute to the thermal transport in bulk Si, are successfully inhibited, leaving the electronic properties largely unaffected. This allows for higher ZT, improved TE efficiency, and makes nano-structured Si an attractive TE material. Subsequently this finding has been corroborated by several research teams worldwide, through both theoretical and experimental studies. The majority have looked to three parameters for SiNW optimisation [4-8] - (i) reduced SiNW diameter, (ii) increased SiNW surface roughness, and (iii) longer wire length. Theoretically, best performance arises for long, rough SiNWs with diameter <10 nm [4], however this geometry is hindered by practical problems such as dopant deactivation, low wire packing density and susceptibility to SiNW breakage and device failure [5,6]. So far only lab-scale demonstrator devices have been validated.

Nano-films

An alternative approach – and one which overcomes some of the practical challenges associated with long, thin SiNWs – is to use Si nano-films, i.e. films that are macroscopic in two dimensions but have thickness at the nano-scale, such as silicon-on-insulator (SOI) films [9]. These are more robust, have better area coverage and are usually manufactured in a more scalable process than SiNWs. However, the major drawback until now has been that the nano-film geometry is far less effective at reducing κ and so TE performance is significantly less for nano-films than it is for SiNWs [10]. Improved performance is possible in nano-films that are decorated with a high density of nanoscopic holes [11] or by phononic-crystal patterning [12]. Unlike the method we introduce here, the electrical properties of these 'holey' films deteriorate significantly with high porosity. Likewise, their porosity makes them fragile to handle, and given they are sensitive to variations in hole size/spacing, are more difficult to reliably fabricate at scale, with hole densities required of 10^{10}-10^{11} cm^{-2} (estimated from [13]).

Vacancy-engineering

In this *communication* a method is described to reduce κ in Si nano-films by $\sim$90% compared to control samples, giving $ZT=0.2$ at 360 K. Crucially, unlike SiNWs or holey Si, our process leaves the Si structure almost indistinguishable from bulk Si and is more straight-forward to fabricate. Unlike other approaches that rely on nano-dimensions for their success, this method can be scaled to microscopic dimensions, and potentially beyond. Bulk properties of Si such as Seebeck coefficient, electrical resistivity, dopant activation, and electron mobility are largely retained, but with vastly reduced κ. This is done by creating vacancy-rich Si via a process of *vacancy-engineering*.

Theory

Vacancies (V) are simple, intrinsic point-defects, which in basic form, are a missing Si atom within an otherwise tetrahedrally coordinated lattice [14]. This is in contrast to their counterpart – the self-interstitial (I) – which, for simplicity, can be considered as an extra Si atom in the lattice. Around a vacancy, lattice relaxation occurs, creating a lattice contraction [14] and additional scattering sites for phonons. Their presence can therefore influence thermal transport, however the equilibrium concentration of vacancies is extremely low in regular Czochralski-grown Si ($<10^{11}$ cm^{-3} [14]) creating negligible impact. Large vacancy concentrations (1.5%) have been calculated theoretically to have a significant impact on the thermal conductivity of bulk Si, reducing κ by up to 95% at 300 K [15-17]. This is explained by increased phonon scattering and a reduction in the mean-free-path length for phonons, due to the relatively high concentration of vacancy defects. However, the vacancy concentration required theoretically, equivalent to $\sim10^{21}$ cm^{-3}, is significantly at odds with the equilibrium vacancy concentration in practice. With vacancy-engineering it is possible to close this gap by artificially creating a super-saturation of vacancies, using self-implantation of Si ions to introduce high vacancy concentrations (0.1–4%) in the near-surface of Si nano-films. This approach has been previously successful in overcoming the problem of transient-enhanced boron diffusion in Si transistor devices [18].

Design

Monte Carlo simulation software was employed to simulate a range of experimental conditions (different ion-energies/SOI substrates) to investigate the spatial distribution of point-defects (both vacancies and interstitials) created by ion-implantation of SOI. Ion-implantation was chosen as the method for vacancy introduction, since it gives controllable and repeatable results, and is a staple technique applied for Si technologies. SOI with a 100 nm-thick Si film and 200 nm-thick buried oxide was chosen for this experiment, with the oxide forming a physical barrier separating net vacancy and net interstitial concentrations from recombining during annealing, and allowing for straight-forward characterisation of the isolated top-layer. The "Stopping and Range of Ions in Matter" (SRIM) code [19] was used for the simulation to extract depth-concentration distributions of vacancy defects ($V(x)$), interstitial Si defects ($I(x)$) and implanted Si ions ($Si(x)$). The net defect distribution ($C(x)$) was calculated as $C(x)=Si+I-V$ [20], a modified version of the Net Recoil Density algorithm [21]. Here a net-positive value indicated a region of interstitial-rich material, and a net-negative value a vacancy-rich region.

Results and discussion

Figure 1 shows the simulated defect depth-concentration distribution for an ion-implanted SOI substrate (100 nm Si/200 nm SiO_2/300 μm Si). A high concentration ($>10^{21}$ cm^{-3}) of vacancy defects is found immediately below the Si surface, which falls to a plateau at depths between 25 and 100 nm, where the vacancy concentration varies between 10^{19}-10^{20} cm^{-3}. Integrating under the curve for depths 0-100 nm gives a net vacancy density of 7.94×10^{14} cm^{-2}, which equates to an average concentration of 7.94×10^{19} cm^{-3} or $\sim$0.16%, though the vacancy concentration reaches 4% in the top 10 nm of the nano-film. While the simulation considers mono-vacancies, known to be mobile at room temperature, di-vacancies and small vacancy-clusters – stable at ambient temperature – are likely to be present with an equivalent depth distribution [22,23]. A relatively high implant fluence of