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Optical second harmonic generation studies of epitaxial growth of Si and SiGe

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Abstract

Optical second harmonic generation (SHG) from Si surfaces has the advantage of surface sensitivity and can be applied in-situ during epitaxial growth process such as gas source molecular beam epitaxy (GSMBE) or chemical vapour depositions (CVD). This enables a number of processes occurring on the surface during epitaxial growth to be investigated in real time. Two processes are of particular interest in the epitxial growth of Si and SiGe structures: (1) oscillatory processes on the surface due to layer-by-layer growth for growth rate measurements and (2) surface segregation of Ge during formation of Si/SiGe heterojunctions. In this paper, we report on the oscillatory SHG response from the Si(0 0 1) surface during homo-epitaxy of Si and variations of SHG response across the SiGe/Si heterojunction during GSMBE growth. The oscillatory response is attributed to the domain coverage variation during layer-by-layer growth analogous to the origin of reflectance anisotropy oscillations. The changes in SHG during formation of SiGe/Si heterojunction is attributed to the gradual variation of surface Ge concentration due to segregation of Ge. The contribution from buried interfaces is shown to be negligible at the photon energy used. © 2000 Elsevier Science B.V. All rights reserved.

Epitaxial growth of thin films is a vital step in the manufacture of heterojunction bipolar transistors and heterojunction MOS devices based on the Si/SiGe material system. However, many growth techniques suffer from a lack of in situ probes which are both surface and compositionally sensitive. Optical second harmonic generation (SHG) is ideally suited for this role as it is both non-invasive and surface sensitive and, as will be shown, sensitive to the composition of the surface in the case of epitaxal growth of Si/SiGe films. This enables the layer-by-layer growth process [1] and Ge surface segregation [2,3] to be investigated in real time. In this work, observation of SHG response from Si and SiGe alloy surfaces is reported and it is used to study the formation of the heterojunction during gas source molecular beam epitaxy (GSMBE).

Optical SHG has an intrinsic surface sensitivity when applied to Si where bulk dipole contribution to the SHG response is forbidden by the inversion symmetry in the solid [4,5]. At the surface, where

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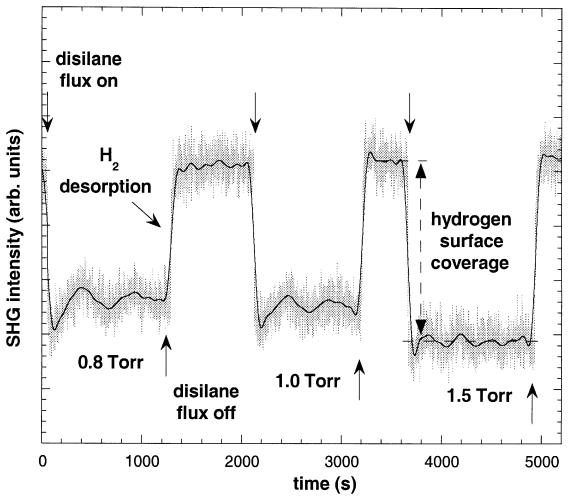


Fig. 1. SHG response from Si(0 0 1) surface during growth at 510°C.

inversion symmetry is broken, surface dipoles are the main contributor to the SHG response in addition to bulk quadrapole and higher-order terms. The SHG response from Si surfaces is increasingly well understood, in particular, at two photon energies of 2.9–3.5 eV [6,7]. The experiments here were carried out at 3.1 eV using a Spectra Physics Millenia pumped Ti : Sapphire laser system. Pulse energies were 8 nJ and pulse duration was of the order 100 fs. The primary radiation of 800 nm was p-polarised and incident on the sample surface at an angle of incidence of 10°. The sample manipulator allows selection of appropriate incident azimuth which is determined from reflection high-energy electron diffraction (RHEED) measurements. Epitaxial growth was carried out on boron doped ($\rho < 1\ \Omega$) norminally singular Si(0 0 1) wafers. They are prepared by ex situ wet chemical etching with a final HF dip to form a hydrogen terminated hydrophobic surface before loading into the growth chamber via interlock and preparation chamber. Disilane (Si_2H_6) and germane (GeH_4) gases were used for film growth.

Fig. 1 shows the SHG response obtained from the surface with the beam incident along the [1 1 0] azimuth at 510°C. The initial decrease in the intensity at the commencement of growth is associated with the increase in surface hydrogen concentration. The change is also larger for a higher disilane flux and this is attributed to a higher steady-state hydrogen coverage on the surface, determined by the competition between the rate of dissociative chemisorption of disilane and the recombinative desorption of molecular hydrogen [8]. The subsequent oscillatory SHG behaviour is attributed to layer-by-layer growth. The association with growth is supported by change in the period of intensity oscillations with different disilane incident flux. The growth rate is clearly faster with a larger incident flux. This periodic variation is particularly pronounced, especially when the surface is first annealed to high temperature (800°C) prior to growth. Ex situ XRD measurement of layer thicknesses and RHEED intensity oscillations measurement revealed that the period of optical SHG oscillations are associated with bi-layer growth period analogous to RAS oscillations [9].

The origin of the observed SHG intensity oscillations is likely to be associated with an anisotropic SHG response from the Si–Si dimers that are orientated parallel and perpendicular to the plane of incidence. In this case, a peiodic domain coverage variation of the (2X1) and (1X2) surface reconstruction during 2D layer-by-layer growth would explain the observed bi-layer SHG oscillations. Alternatively, it is also possible for the anisotropic SHG response to arise from steps. The density of steps with a particular orientation would change at a bi-layer frequency during 2D layer-by-layer growth and would therefore provide the same oscillatory behaviour. However, the significant change in SHG response induced by the presence of hydrogen on the surface, suggest that the SHG response is largely derived from the terrace of the surface (saturation of dangling orbitals) and the oscillatory response observed is more likely to be associated electronic states of the dimers on the terraces. Hence, the argument based on domain coverage is the more likely cause of the oscillatory SHG response. SHG intensity oscillations thus provide an alternative measure of the Si epitaxial growth rate, particularly in situation such as CVD where high pressure prevents use of techniques such as RHEED intensity oscillations.

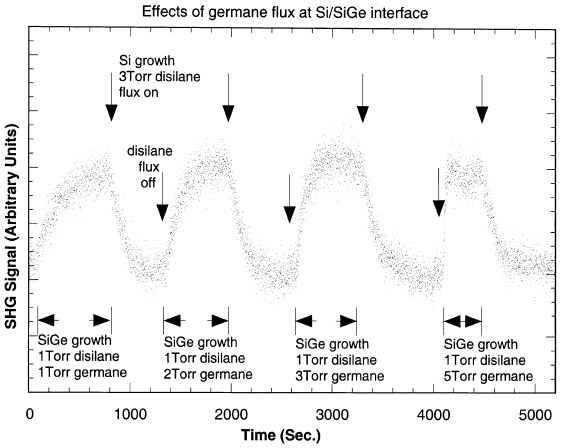


Fig. 2. SHG response from the surface during formation of SiGe/Si heterojunction of different Ge compositions at 650°C.

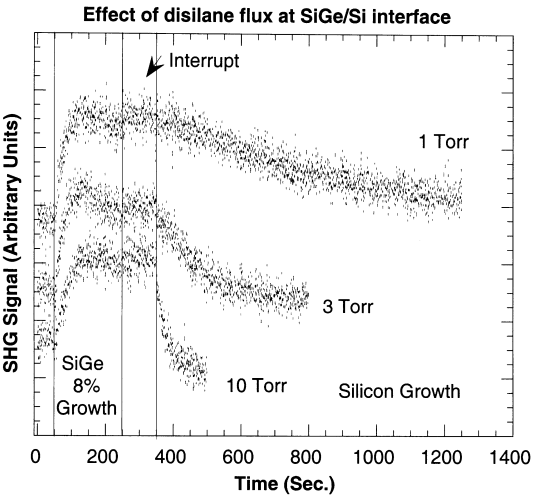


Fig. 3. SHG response from the surface during formation of SiGe/Si heterojunction at 650°C as a function of disliane flux in the capping layer.

Apart from growth rate measurements and the sensitivity to the presence of hydrogen on the surface, SHG response was also investigated during in situ heteroepitaxiy of Si/SiGe and SiGe/Si. Fig. 2 shows the SHG signal from the surface during growth of a Si/SiGe heterojunction on a Si(0 0 1) substrate at 650°C. The higher substrate temperature reduces the mono-hydride coverage on the surface and hence its effect on the SHG response. The sensitivity of the technique to the presence of Ge is clearly seen from the change in the SHG signal induced when the growth of SiGe (an increase of SHG signal) is initiated on the clean Si surface. The SHG eventually settles to a steady-state signal corresponding to steady-state growth of SiGe. After the SiGe layer is buried by further deposition of silicon, the SHG signal returns to that of a clean Si surface. While the presence of interfaces and Ge break the local inversion symmetry and can in general generate a SHG response, buried SiGe layers and SiGe/Si interfaces, clearly do not make a significant contribution to the observed SHG signal. This is perhaps expected given the entirely different local bonding arrangement between a reconstructed surface and a fully coordinated buried interface. The SHG response at the wavelength of 800 nm is thus only sensitive to processes that occur on the surface. The time evolution of the SHG signal hence gives an indication of time evolution of the surface Ge concentration during the formation of Si/SiGe heterojunctions. In particular, the time taken to reach a steady state SHG signal at the start of SiGe growth is much shorter with a higher germane over pressure (Fig. 2). While this does not directly indicate a more abrupt interface, the relative small effect of growth rate enhancement at high temperature [10] means the same conclusion can still be obtained taking into account the small growth rate changes between the different incident germane fluxes.

The optimisation of the Si/SiGe interface has not been considered extensively and the influence of the germane over pressure is often considered sufficient to produce sharp interfaces. However, the SHG results indicate otherwise. Tensile strained Si two-Dimensional electron gas (2DEG) structures were grown with pre-deposited Ge at the Si/SiGe interface to optimise interface sharpness. Preliminary transport measurements indicate a 15% increase in low-temperature mobility. Similarly, optimisation of the SiGe/Si interface is also important, since the abruptness of this interface has a strong influence on the transport properties of two- dimensional hole gas structures. Fig. 3 shows the dependence of SHG signal during the formation of the SiGe/Si

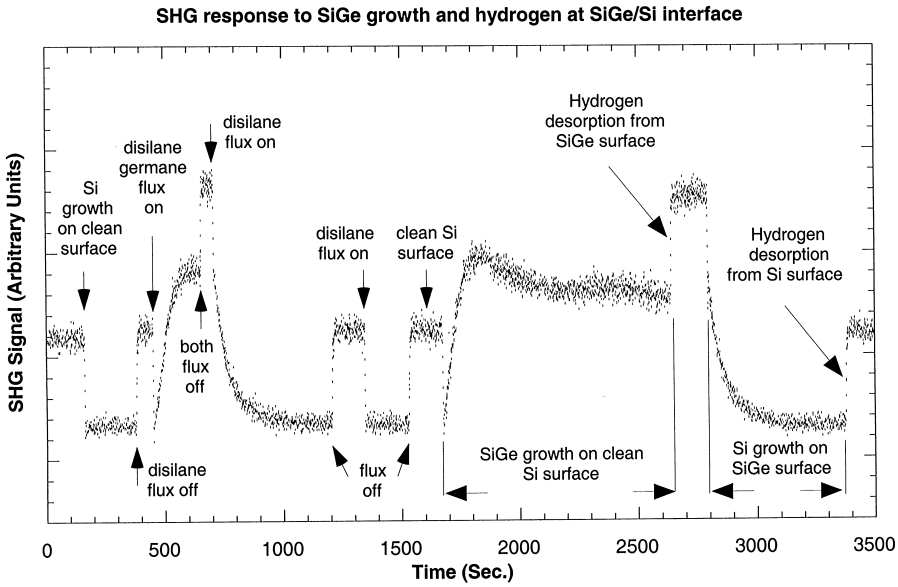


Fig. 4. SHG Response from the surface during formation of SiGe/Si heterojunction at 560°C.

interface as a function of the disilane source pressure at substrate temperature of 650°C. Under the growth condition, the growth rate is supply rate limited and the surface is free from hydrogen coverage. Taking into account on the growth rate differences, the different gradient observed in the figure would again indicate the difference in degree of abruptness of the interface formed during growth. In particular, a more abrupt interface is achieved with a higher disilane over-pressure, which is consistent with recent SIMS and RHEED investigations [11].

During GSMBE growth, it is generally believed that adsorbed hydrogen at the surface passivates the surface dangling bonds and thereby suppressing Ge segregation. However, in the temperature range studied here, the coverage of hydrogen is expected to be significantly smaller and it is likely that the segregation will occur freely over the *bare* surface Si surface. The more abrupt interface (i.e. less Ge segregation) observed with a higher disilane flux would therefore imply a growth rate effect related to a burying effect that block the bare surface sites and hence suppressed the segregation, i.e. the interchange between Si and Ge at the surface and subsurface layer. This effect is thus not due to the presence of hydrogen on the surface. Similar effect of growth rate dependence in Ge surface segregation during solid source MBE has been reported by Nakagawa et al. [12] in 1997 using XPS measurements.

Fig. 4 shows the SHG signal from the surface during growth of Si/SiGe heterojunctions on Si(0 0 1) substrate at 560°C. At this lower growth temperature, hydrogen present on the surface would also induce changes in the SHG signal [13,14]. While this would mask the changes induced by the presence of Ge, the time evolution of the SHG response to establishing a steady-state surface concentration of Ge and hydrogen is clearly different and therefore would still allow us to assess the quality of the interface.

Time-resolved optical SHG is thus a suitable in situ probe for studying and monitoring the formation of Si/SiGe or SiGe/Si interfaces. In the present work, sensitivity of SHG to surface Ge concentration and application to the optimisation of growth conditions for silicon and germanium-based device structures are demonstrated. More quantitative and spectroscopic work is underway to establish

resonance and make comparisons with the models of segregation process.

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