Supporting Information

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SI Text

Methods. Second harmonic generation. A schematic illustrating our second-harmonic generation (SHG) configuration is given in Fig. S1. Experiments are performed in the reflection geometry using p- [transverse-magnetic (TM-)] polarized 100-fs pulses from a Ti:sapphire oscillator. The wavelength is centered at 810 nm, and the repetition rate is 76 MHz. The pulses are focused onto the sample at a 45° angle of incidence in the laboratory frame. A glass filter eliminates the fundamental in the reflected beam. A polarizer following the glass filter prevents any residual s- [transverse-electric (TE-)] polarized light from reaching the detector. The detector is a photomultiplier operating in a photon-counting mode. The sample is rotated in 1° increments over a 360° range, with each 360° scan taking 98 s. The beam is aligned to trace a 4-mm diameter circle during rotation to ensure that laser-induced heating or charging effects are avoided.

Spectroscopic ellipsometry. Spectroscopic ellipsometric data were obtained with a previously described spectroscopic ellipsometer (1) modified for rotating-compensator operation. Data were obtained with the polarizer and analyzer at an azimuthal angle of 30°. The angle of incidence was 67.08°. The calculated spectral dependences of the changes expected in the C₂, S₂, C₄, and S₄ coefficients of the \( \cos(2\omega t) \), \( \sin(2\omega t) \), \( \cos(4\omega t) \), and \( \sin(4\omega t) \) harmonics, respectively, of the detected intensity are shown in Figs. S2a and b for 0.1-nm-thick overlayers of SiO₂ and amorphous Si, respectively.

At 2.83 eV these changes are specifically \( \Delta C_2 = +0.00743 \) and \( -0.00093 \) for SiO₂ and amorphous Si, respectively, as indicated by the red and brown dots, respectively. The changes \( \Delta S_2 \) are negligible. At the same energy the changes \( \Delta S_4 \) are 0.00366 and \( -0.00001 \) for SiO₂ and amorphous Si, respectively, as indicated by similar dots. Hence at 2.83 eV the C₂ contribution originates primarily from SiO₂, whereas that for S₄ primarily from amorphous Si. This provides the opportunity to assess how the SiO₂ overlayer and disordered interface layer evolve with oxidation, assuming that the respective dielectric responses can be modeled by SiO₂ and amorphous Si. The assumption for SiO₂ should be good to a high degree of accuracy. That for the interface could be debated, because the dielectric response for the disordered Si at the Si–SiO₂ interface will probably be somewhat different. However, we believe that this is a good first approximation (2). If anything, it is likely to underestimate the actual interface thickness.


Fig. S1. SHG configuration. Pulses centered at 810 nm from a Ti:sapphire oscillator are divided into two paths by the beam splitter. The sample is excited at a 45° angle of incidence. The SHG signal is normalized against long-term intensity fluctuations by the signal from the quartz crystal.

Fig. S2. (A) Calculated changes from 1.5 to 6.0 eV expected in the \( \cos(2\omega t) \) and \( \sin(2\omega t) \) coefficients of the intensity measured with a rotating-compensator ellipsometer, caused by the addition of 0.1-nm overlayers of SiO₂ and amorphous Si on a crystalline Si substrate, as indicated. (B) As A, but for the \( \cos(4\omega t) \) and \( \sin(4\omega t) \) coefficients.