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Surface Science 583 (2005) 80–87
SURFACE SCIENCE
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Band bending at the Si(1 0 0)–Si_3N_4 interface studied by photoreflectance spectroscopy

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Received 21 December 2004; accepted for publication 16 March 2005
Available online 7 April 2005

Abstract

Photoreflectance spectroscopy has been used to measure the band bending at the p-Si(1 0 0)–Si_3N_4 interface subjected to annealing and ion implantation. Upon annealing, unimplanted interfaces exhibit a constant band bending of about 0.77 eV, even though the spectral amplitude changes due to variations in the way minority carriers are annihilated at the interface. Implantation reduces the band banding, although subsequent annealing in stages up to 900 °C progressively restores the bending to its original value through pathways exhibiting a wide range of activation barriers.

Keywords: Silicon; Silicon nitride; Interface; Photoreflectance spectroscopy; Band bending; Defects

1. Introduction

Interfaces of silicon with dielectrics appear widely in microelectronic devices and therefore have attracted considerable study. Electrically active defects at such interfaces—particularly Si–SiO_2—have garnered particular attention because of the role such defects play in degrading device behavior. Si–SiO_2 interfaces can be fabricated with very few defects, but processing steps such as ion implantation or X-ray lithography can induce substantial defect formation. The formation and disappearance of such defects [1–6] has been studied in considerable detail, with most attention focusing on the so-called "P_b center" [7,8]. Other kinds of defects can form, however, particularly in response to ion implantation. In contrast with P_b centers, whose concentrations evolve quickly at temperatures around 600 °C, some defects require temperatures up to 1000 °C to evolve at similar rates.

This laboratory has examined the behavior of such defects formed by sub-keV Ar^+ bombardment at Si(1 0 0)–SiO_2 [9] and the Si(1 1 1)–SiO_2 interfaces [10]. The bombardment led to a band bending ~0.5 eV at both the interfaces, and upon annealing, both interfaces exhibited two kinetic regimes for

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doi:10.1016/j.susc.2005.03.026

the evolution of band bending due to defect healing. Such defect-induced band bending was shown in subsequent simulations of pn junction formation to persist throughout typical short-time annealing steps after implantation and to have significant effects on junction depth [11]. The atomistic mechanism responsible for defect healing remained unclear, though unusually low activation energies (less than 1 eV) for band bending evolution suggested that a distribution of energies was involved.

The present work represents an attempt to better understand the mechanism for defect healing by examining an analogous interface of Si–Si_3N_4. There already exists some literature documenting the behavior of Si–Si_3N_4. For example, interface trap densities have been obtained by capacitance–voltage measurements for nitride grown by photochemical vapor deposition [12] and jet vapor deposition [13,14]. A charge pumping technique has been used to determine the trap densities at the same interface where thermally grown nitride films were used as gate insulators of MISFET transistors [15]. As in earlier reports [9,10] for Si–SiO_2, the present work employs optical technique of photoreflectance to examine the evolution of band bending in response to low-energy ion implantation.

2. Experiment

Photoreflectance (PR) is one of a class of modulation spectroscopies in which a semiconductor is periodically perturbed, and the resulting change in dielectric constant is detected by reflectance [16,17]. PR accomplishes the modulation with a chopped laser beam having hv greater than the fundamental bandgap energy E_g. Photogenerated minority carriers migrate to the interface and recombine with charge stored there. The resulting change in built-in field affects the surface reflectance R in narrow regions of wavelength corresponding to optical transitions of the substrate material. The small reflectance change $\Delta R/R$ exhibits a spectral dependence that is monitored with a weaker, independent probe beam using phase sensitive detection. The presence of a nonzero PR spectrum demonstrates unequivocally the existence of surface band bending, and experiments as a function of temperature and pump intensity can yield useful estimates of the degree of this band bending [18].

Experiments were performed in a turbomolecularly pumped ultrahigh vacuum chamber set up in conjunction with optics for PR as described elsewhere for a similar system [17]. Base pressures in the low 10^{-9} Torr range were regularly achieved. The chamber was equipped with a variable energy ion gun (up to 2.0 keV) for ion implantation and Auger electron spectroscopy (AES) for surface characterization. Samples of dimensions 1.7 cm × 0.7 cm were cut from boron doped Si(1 0 0) wafers with resistivity of 0.014 Ω cm corresponding to a doping level of 1×10^{18} cm^{-3}. Resistive heating of samples was employed, with temperature monitored by a chromel–alumel thermocouple. A He–Ne laser operating at 632 nm served as the pump beam. Spectra were collected at 302 K (unless otherwise specified) in the vicinity of the nearly degenerate E_1 and E_0' [19] optical transitions of Si, which lie near 3.4 eV.

Clean Si(1 0 0) surfaces were obtained by removing native oxide with aqueous HF, quickly transferring the sample to the vacuum chamber, baking to achieve ultrahigh vacuum, and heating the surface at 850 °C for 5 min. AES revealed less than 3% contamination with C and O after this treatment. Nitrided surfaces were prepared by exposure to 3×10^{-6} Torr of ammonia for 10 min at 800 °C. AES scans showed that this procedure resulted in the formation of about 1.2 monolayers of silicon nitride. After nitridation, samples were implanted with 1.0 keV Ar ions. We used Ar to induce interface bond breakage without intentionally affecting the doping level of the underlying Si, which affects both the amplitude and the lineshape of the PR spectra and therefore complicates data interpretation. An ion fluence of $1 \times 10^{15}/cm^2$ was used in all experiments reported here.

3. Results

3.1. Band bending after thermal nitridation

Fig. 1 shows room temperature raw PR spectra at various illumination intensities for thermally