DTU Library

Fusion bonding of Si wafers investigated by x ray diffraction

Weichel, Steen; Grey, Francois; Rasmussen, Kurt; Nielsen, Mourits; Feidenhans'l, Robert Krarup; Howes, Paul; Vedde, J.

Link back to DTU Orbit

Fusion bonding of Si wafers investigated by x ray diffraction

S. Weichel, F. Grey, and K. Rasmussen
Mikroelektronik Centret, Technical University of Denmark, DK-2800 Lyngby, Denmark

M. Nielsen,[a] R. Feidenhans'l, and P. B. Howes
Risø National Laboratory, DK-4000 Roskilde, Denmark

J. Vedde
TOPSIL Semiconductor Materials A/S, DK-3600 Frederikssund, Denmark

The interface structure of bonded Si(001) wafers with twist angle 6.5° is studied as a function of annealing temperature. An ordered structure is observed in x-ray diffraction by monitoring a satellite reflection due to the periodic modulation near the interface, which results from the formation of a regular array of screw dislocations. This satellite reflection first appears at an annealing temperature of 800 °C, and increases abruptly up to temperatures of 1000 °C. We propose that this transition occurs when there is sufficient mobility for the reorganization of atomic steps and terraces in the interface region. © *2000 American Institute of Physics.* [S0003-6951(00)03401-X]

Fusion bonding of wafers without any intermediate adhesive layer has become an important fabrication technique in semiconductor technology.[1] The mechanism for bond formation during the annealing process has recently been discussed by Tong and Gösele.[1] Strong bonding is obtained both between oxidized hydrophilic Si surfaces and between hydrogen terminated hydrophobic Si surfaces. While the hydrophilic surfaces produce an amorphous interface layer of SiO_2 after annealing, the hydrophobic Si surfaces result in covalent Si–Si bonds at the interface as in bulk crystals. The interface bond energy of the hydrophobic Si/Si wafers has been measured[2] by the crack opening method[3] as a function of annealing temperature. The bond energy increases for temperatures above 300 °C and full strength is achieved above 700 °C, when sufficient time of annealing is allowed for equilibrium to be reached. Four temperature intervals have been suggested. Below 150 °C the room temperature bonded structure is stable. It is achieved by contacting the prepared hydrophobic wafers under clean conditions and with a moderate pressure. Recent calculations[4] suggest that the bonding forces in this regime are long-range van der Waal forces between the outermost Si atoms, which are kept apart by repulsive forces between the adsorbed hydrogen atoms. Next, between 150 and 300 °C the bond energy increases slowly, possibly due to diffusion of weakly bound surface contaminants or formation of H–F–H or H–O–H bridges between the wafers. From 300 to 700 °C hydrogen desorbs and covalent Si–Si bonds are formed. Finally, above 700 °C diffusion of Si atoms at the interface occurs possibly influenced by the presence of hydrogen,[1] and thereby remaining nanoscale gaps at the interface are sealed and an interface is obtained with a bond strength comparable to bulk silicon.

In previous x-ray diffraction measurements[5] we have characterized the atomic interface structure of fusion-bonded Si(001) wafers annealed at 1100 °C, and we have shown experimentally that for twist angles θ less than 8°, the interface is well described by a model where the atomic displacements are determined by a square net of screw dislocations. This model represents the generally accepted idealized picture of grain boundaries with zero tilt but finite twist misalignments.[6–8] The net of screw dislocations results in a periodic modulation of atoms from their bulk positions, and we observe[5] that this modulation extends into the bonded crystals to a depth inversely proportional to the twist angle. In the present work we have measured the diffraction signal due to the periodic modulation at the interface on a series of samples with identical twist angles of $\theta = 6.5°$ but annealed at different temperatures. We observe an abrupt onset of the diffraction signal from the ordered interface structure at $T = 800$ °C.

The samples were prepared as follows. Two double side polished, 4 in. diameter, Si wafers of nominal thickness 350 μm were stripped of their native oxide and hydrogen passivated by dipping 20 s in a 5 wt. % hydroflouric acid solution. The wafers were used as delivered from the manufacturer and no other pretreatment was made. The hydrophobic wafers were then contacted in a clean room at a twist angle $\theta = 6.5°$ at room temperature. The resulting contact-bonded wafer pair was mounted in a single side etching holder which uses an O-ring sealing mechanism so that one wafer can be chemically thinned while keeping the other intact. The exposed wafer was thinned to less than 30 μm using a timed etch stop in potassium hydroxide at 80 °C. Although such contact-bonded wafers are not normally strongly enough bonded to be mechanically diced, we found that the thinning procedure made the wafer pair considerably more robust. This is presumably because the thinned wafer is more elastically compliant, resulting in a more conformal interface and hence a stronger bonding of the wafer. As a result 1 cm^2 chips suitable for mounting on the diffractometer could be prepared under identical bonding conditions and could be annealed individually at different temperatures under flowing nitrogen atmosphere. The temperature was ramped up and

---

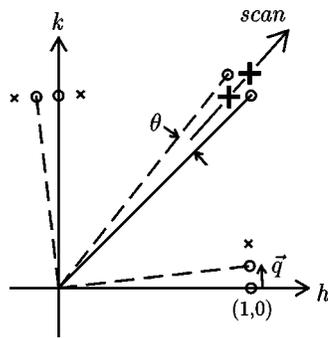[a] Electronic mail: mourits.nielsen@risoe.dk

     70

FIG. 1. The figure shows the reciprocal lattice plane (hk) parallel to the interface plane of the bicrystals with twist angle $\theta = 6.5°$, in surface coordinate notation (see Ref. 10). The vector $\vec{q}$ joins the $(1\ 0\ l)$ points of the two crystals, and the crosses (small and big) show some satellite positions, displaced from bulk Bragg points by $\vec{q}$ or its symmetry equivalents. The big arrow indicates the scans of Fig. 2 through the satellites shown by big crosses +.
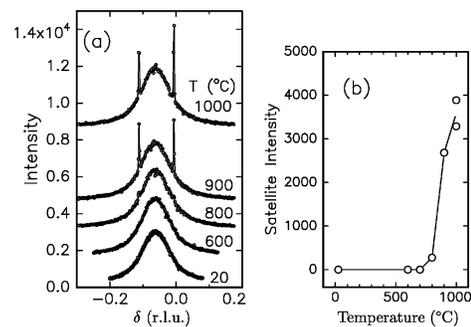

FIG. 2. (a) X-ray diffraction profiles from the Si(001) bicrystals annealed at increasing temperatures T as noted in the figure. The profiles are measured in radial scans with coordinates $(1+\delta, (1+\delta)1.12, 2)$, and varying δ as indicated by the big arrow in Fig. 1. For clarity the measured curves are displaced vertically relative to each other. (b) Variation of the satellite intensity at the positions indicated by + in Fig. 1, as a function of on the annealing temperature.

down at 1 °C/s, and the maximum annealing temperature, T, was maintained for 15 min.

The x-ray diffraction measurements were performed at ESRF at the undulator beam line ID32. The diffractometer is a vertical scattering instrument which allows out of plane setting of both the incoming and the scattered beam.[9] This is important in order to keep the attenuation in the top crystal low and, hence, to be able to measure the structure of the buried interface. The x-ray energy was 21 keV, the angles of the two beams to the surface were between 3° and 9°, and so the total attenuation by absorption in the top wafer was kept below 50%. The samples were oriented on the diffractometer with the (001) axis parallel to the common axis of the sample rotation ω, and the detector arm 2θ. We use the conventional coordinate notation for surface structure studies,[10] where h and k denote the momentum transfers parallel to the surface in units of $(2\pi/a)\sqrt{2}$, l denote perpendicular momentum transfer in units of $2\pi/a$, where $a = 5.43$ Å is the cubic lattice constant of Si. Scans are performed in h and k coordinates keeping l constant.

When the strong covalent bonding between the two crystals is formed, the atoms near the interface become displaced with an in-plane periodicity d given by[7]

$$d = (a/\sqrt{2})/[2\sin(\theta/2)],$$

where θ is the twist angle. The direction of the atomic displacements is predominantly parallel to the interface, and the amplitude decays exponentially away from the interface. The fundamental satellite wave vector corresponding to the first harmonic of the periodic modulation is given as the vector $\vec{q}$ between the (101) reciprocal lattice points of the two crystals[10] as shown in Fig. 1. We determine the dependence of the periodic modulation on the annealing temperature by measuring the intensity of the satellite reflections by x-ray diffraction. The radial scan shown by the big arrow in Fig. 1 includes the two satellites shown by big crosses displaced $\vec{q}$ and $-\vec{q}$ from the (112) Bragg points of the crystals.[10]

The resulting scattering profiles are shown in Fig. 2(a). The dominant broad peak is thermal diffuse scattering and defect scattering, which peaks at the bulk Bragg points. The scattering signal from the periodic modulation is the two sharp satellite peaks at (0.887 0.994 2) and (0.994 1.113 2),

indicated by the big crosses in Fig. 1. Figure 2(a) demonstrates the onset of the periodic modulation at annealing temperatures of 800 °C. The width of the satellite reflections is small and constant and given by the instrumental resolution, which is determined by the slits on the detector arm. In the transverse direction the resolution of the instrument is much higher and the measured widths correspond to ordering of the periodic modulation with a coherence length exceeding 1 μm. In the l direction perpendicular to the h,k plane the satellite scattering intensity peaks at $l=2$ and has, as function of l, a full width at half maximum of 0.29 reciprocal lattice units, which means that for the twist angle $\theta = 6.5°$ the exponential decay length of the periodic modulation is about 4 Å.[5]

Figure 2(b) summarizes the annealing data and shows the abrupt onset of the integrated signal, at the satellite positions, when T exceeds 800 °C. We identify the satellite scattering intensity with the presence of a covalently bonded interface with an ordered periodic structure. Quantitatively, we cannot determine whether the entire interface area has this quality. A fraction of the interface may remain disordered or may not bond, and will then not contribute to the satellite signal after annealing at the highest temperatures. At the microscopic scale, such voids are known to exist.[1]

It is remarkable that within the resolution of our experiment, the width of the satellite peaks in Fig. 2(a) does not depend on the annealing temperature. The simplest explanation for this is to assume that the scattering intensity reflects area of the interface that are covalently bonded and ordered, and that once such an area nucleates, it grows spontaneously to a size larger than the 1 μm spatial resolution of the diffractometer. As annealing proceeds to higher temperatures, the fraction of the surface where this nucleation and growth has occurred increases steadily.

We can compare the result in Fig. 2(b) with the data for the bond strength as function of annealing temperature measured by Tong *et al.*[2] Two factors complicate the comparison: first, the annealing times in the two experiments are different (1 h at highest temperature versus 15 min in our experiment); second, the bond strength measurements do not extend to the highest annealing temperature, because the crack opening method does not allow the maximum strength to be measured.

We observe that the periodic modulation characteristic of a well-ordered interface structure appears at 800 °C and continues to increase up to 1000 °C. On the other hand, Tong *et al.* observe bond strengths characteristic of a fully covalently bonded interface already at 700 °C. To explain this difference, we propose that while covalent bonding is achieved once hydrogen desorption and diffusion away from the interface has occurred, crystallographic ordering of the interface requires higher temperatures where significant diffusion and reordering of the atomic terraces and steps at the interface can occur. To support this proposal, we note that atomic terraces of area 10^5 nm^2 on Si(001) disappear by Ostwald ripening on time scales of minutes at 820 °C.[11] Dissolution of much larger features, of order 10^8 nm^2 , occurs on a similar time scale at 950 °C.[12] On Si(111), the transition from 7×7 reconstruction to ''1×1'' phase occurs at 860 °C, and is associated with a considerable increase in surface diffusion of adatoms and step motion.[13] Thus, 800–1000 °C corresponds to the temperature range in which major rearrangement of the interface structure can occur on the 10 nm–10 μm length scales, within time intervals relevant to our experiment. In contrast, local rearrangements of adatoms[14] or vacancies[15] at Si(001) surface occur on the same time scale at temperatures in the range 400–600 °C. Thus, while local covalent bonding may be achieved in this temperature range, and could account for the large bond strengths measured after annealing at 700 °C, global ordering of the interface appear to require annealing at significantly higher temperatures.

In conclusion, by x-ray diffraction and using a simple thinning procedure, we observe diffraction due to the periodic modulation that occurs at the interface between two Si(001) wafers, as a function of the annealing temperature of the wafer pair. The onset of this interface structure occurs abruptly at about 800 °C, nucleating in patches that grow rapidly to sizes $>1\,\mu$m. We propose that this transition coincides with a temperature range where diffusion of steps and atomic terraces allows major rearrangements of the interface to occur, resulting in a crystallographically ordered interface.

[1] Q.-Y. Tong and U. Gösele, *Semiconductor Wafer Bonding* (Wiley, New York, 1999), pp. 117–122.

[2] Q.-Y. Tong, E. Schmidt, U. Gösele, and M. Reiche, Appl. Phys. Lett. **64**, 625 (1994).

[3] M. P. Maszara, G. Goetz, A. Cavilia, and J. P. McKitterick, J. Appl. Phys. **64**, 4943 (1988).

[4] K. Stockbro, E. Nielsen, E. Hult, Y. Anderson, and B. I. Lundquist, Phys. Rev. B **58**, 16118 (1998).

[5] M. Nielsen, R. Feidenhans'l, P.B. Howes, F. Grey, K. Rasmussen, and J. Vedde, Surf. Sci. Lett. **442**, 989 (1999).

[6] J. P. Hirth and J. Lothe, *Theory of Dislocations,* 2nd ed. (Krieger, Malabar, FL, 1982), pp. 703–713.

[7] A. P. Sutton and R. W. Balluffi, *Interfaces in Crystalline Materials*, Monographs of the Physics and Chemistry of Materials, Vol. 51 (Clarendon, Oxford, 1995), pp. 70–148.

[8] C. B. Carter, H. Höll, D. G. Ast, and S. L. Sass, Philos. Mag. **43**, 441 (1980).

[9] R. Feidenhans'l, Surf. Sci. Rep. **10**, 105 (1989).

[10] In measurements of crystalline surface structures by electron-, x-ray or neutron diffraction it is conventional to use a unit cell which, parallel to the surface, is given by the unreconstructed top layer of atoms or molecules. For the Si(001) surface this is given, in bulk notation, by the nearest neighbor cell of the fcc structure, f.ex. $[a/2\ a/2]$ and $[-a/2\ a/2]$ in real space with a being the cubic cell dimension. In reciprocal space the (1 0 l) reflection in surface notation is the bulk (1 1 l) reflection and the surface (1 1 l) is the (2 0 l) bulk reflection.

[11] N. C. Bartelt, W. Theis, and R. M. Tromp, Physica B **54**, 11741 (1996).

[12] S. Tanaka, N. C. Bartelt, C. C. Umbach, R. M. Tromp, and J. M. Blakely, Phys. Rev. Lett. **78**, 3342 (1997).

[13] S.-I. Kitamura, T. Sato, and M. Iwatsuki, Nature (London) **351**, 215 (1991).

[14] Y. W. Mo, J. Kleiner, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **66**, 1998 (1991).

[15] N. Kitamura, M. G. Lagally, and M. B. Webb, Phys. Rev. Lett. **71**, 2082 (1993).