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Ultra long-range interactions between silicon surfaces

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ABSTRACT

This paper takes a new look at interactions between hydroxylated silicon surfaces, which are commonly exploited in wafer bonding. In the past, strong connections have been made between the fracture toughness associated with such interactions. Here, we go one step further to examine the strength and range of the interactions, as well as the fracture energy from the perspective of traction-separation relations and cohesive zone modeling. The surface profiles of the interacting surfaces along with the initially bonded state were characterized by interferometry. The bonded silicon strips were separated by wedge loading while the separation of the surfaces was measured by infra-red crack opening interferometry. This data was used in conjunction with J-integral concepts to extract traction-separation relations directly. Variations in the fracture energy and strength and range of the interactions of a range of samples were linked to the mismatch in the waviness of the contact pairs and the amount of damage this caused. Finally, the strength and range of the interactions of well-bonded samples appeared to be linked to DLVO and capillary effects rather than van der Waals interactions.

1. Introduction

Wafer bonding technology, where two separate wafers are often bonded without additional adhesive agents between them has been a cornerstone of the semi-conductor industry (Plößl and Kräuter, 1999, Christiansen et al., 2006) because it allows for effective interconnection of stacked three-dimensional wafer structures. Our understanding of the chemistry of wafer bonding is quite mature (Plößl and Kräuter, 1999, Christiansen et al., 2006, Tong et al., 1994, Gösele et al., 1995a, Gösele et al., 1995b, Bengtsson et al., 1996, Tong et al., 1997, Tong et al., 1998, Suni et al., 2002, Turner and Spearing, 2002, Miki and Spearing, 2003, Tong et al., 2004, Turner, 2004, Ventosa et al., 2008, Naumenko and Skrypnyk, 2013, Masteika et al., 2014) and fracture mechanics approaches have been used (Plößl and Kräuter, 1999, Christiansen et al., 2006, Turner, 2004, Naumenko and Skrypnyk, 2013, Masteika et al., 2014) to determine the fracture toughness associated with various processing steps such as ambient curing, annealing, plasma treatments, etc. Nonetheless, the strength and range of the interactions between silicon wafers following bonding has received limited attention. Interaction potentials were developed for molecular dynamics simulations of ambient hydrophilic bonding in order to determine the traction-separation relations between water and hydroxylated silicon or native silicon oxide (Cole et al., 2007). The simulations captured the repulsive and adhesive behavior as a function of the separation distance. The maximum interaction range grew to several nano meters as the water coverage or relative humidity was increased. These traction-separation relations were incorporated in a continuum spectral scheme (Geubelle and Rice, 1995) to obtain a resistance curve for the evolution of debonding from initiation to steady state (Kubair et al., 2009) but no comparisons were made with experiments. A traction-separation relation associated with purely capillary effects was developed (Thouless, 1992) based on the separation of two parallel plates joined by a confined liquid film. The meniscus velocity converged to a threshold toughness that was the surface energy of the confined liquid, but the strength and range of the interaction were not quantified. A more general model that accounted for the viscosity of the liquid trapped between bonding wafers was developed on the basis of the Reynolds equation and incorporated (Kubair and Spearing, 2007) in a continuum spectral scheme. The model was unable to capture the adhesive hysteresis (Turner, 2004) noted in wafer bonding and separation experiments, most likely due to the fact that the trapped liquid in the experiments is not continuous as is assumed in the model. These "bottom up" views of traction-separation relations and their continuum level implementations have yet to be compared with "top down" representations based on a continuum perspective of the interactions, thereby further motivating the current study.

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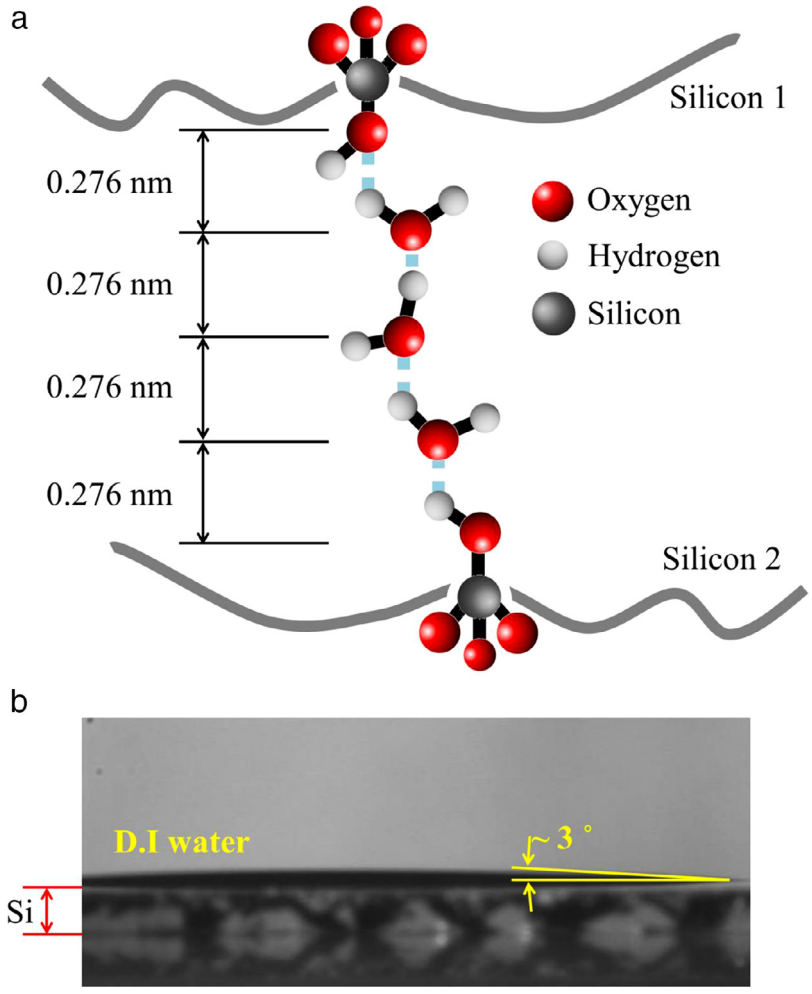

Fig. 1. (a) Schematic of hydrophilic bonding (Tong et al., 1997) and (b) contact of DI water on hydroxylated Si(111).

2. Experiment

Once two hydroxylated silicon wafers are brought into contact and tapped at their center, hydrophilic bonding initiates and propagates uniformly until the entire wafers are bonded; the propagation of the bonding front is known as the bonding wave (Plößl and Kräuter, 1999). This initial bonding can subsequently be strengthened by heating or annealing the assembly. Christiansen et al. and Tong et al. (Christiansen et al., 2006, Tong et al., 1998) reported that the fracture toughness for hydrophilic bonding at temperatures below 100°C was less than 300 mJ/m^2. From 100 to 200°C, the bonding energy increased rapidly to approximately 1200 mJ/m^2 and remained constant up to 800°C. Below 100°C, the main bonding mechanism at the room temperature is hydrogen bonding. Covalent bonding beween silicon and oxygen and the formation of hydrogen gas molecules is dominant at higher temperatures. The range of values reported reflects a number of possible chemical reactions between silicon, oxygen and hydrogen, which are now described in more detail.

The schematic shown in Fig. 1a depicts the situation that first arises when hydroxyl terminated silicon surfaces are brought together in the presence of water molecules. The main interaction at this stage is reversible hydrogen bonding between oxygen and hydrogen atoms. Once heat is applied, the interactions become covalent through the polymerization reaction (Christiansen et al., 2006)

$$\mathrm{Si-OH+OH-Si} \longleftrightarrow \mathrm{Si-O-Si+H_2O}, \tag{1}$$

which is a reversible process below 400°C (Christiansen et al., 2006, Masteika et al., 2014). However, above 400°C, the water molecules produced during polymerization can diffuse through bulk silicon to form silicon oxide and release hydrogen gas through the reaction

$$\mathrm{-Si-Si-+H_2O} \rightarrow \mathrm{-Si-O-Si-+H_2} \tag{2}$$

In this process, the fracture toughness increases by a factor of six over the value at the initial bonding state. In the current work, hydrophilic bonding under ambient conditions is explored in order to understand the role of water molecules between contacting silicon surfaces. Thus hydrogen bonding is expected.

In this work, the initial step in preparing the Si(111) surfaces for bonding was to remove any contaminants. This was followed by a piranha treatment (a mixture of 5 ml of H_2O_2 and 15 ml of H_2SO_4), which results in OH^- termination of the wafer surface. The presence of these hydroxyl groups on silicon wafers gave rise to very strong hydrophilic behavior and very small contact angles (Fig. 1b). The second step was to activate the bonding by bringing two hydroxyl terminated silicon strips into contact. This leads to relatively low fracture energies (Turner, 2004), which can be accommodated for wafer studies, but was difficult for the narrow strips being used in this study. In order to obtain more effective bonding and higher fracture energies, it was necessary to apply a drop of DI water to one strip before bringing the second one into contact and apply a clamp for one minute. Following release, the bonded samples were dried for one day under ambient conditions.

The extent of bonding between the silicon strips was detected by an IR microscope. A panoramic view of a nearly fully bonded sample, using images that were taken by the 2.5× objective lens over the 5×45 mm extent of the silicon strips is shown in Fig. 2a. Only