Fingerprinting bond reactions on vicinal Si(001) by single-wavelength optical second harmonic generation

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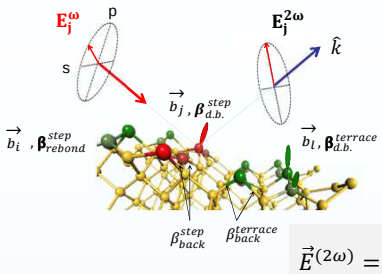
Abstract

Step-edge rebonds and terrace dimers at vicinal Si(001) surfaces provide foundations for growth of nano-wires and epitaxial films, respectively. *In-situ* monitoring of these bonds is important for controlling growth of these structures. Here we fingerprint step rebonds and terrace dimers via the unique rotational anisotropy (RA) of their single-wavelength second-harmonic generation (SHG). Previously RA-SHG was used to monitor backbond-angle distortion at simple surfaces [Si(111)-1x1] with only 4 bonds per unit cell [1]. However, at complex surfaces such as vicinal Si(001), the identifying RA-SHG signature of a single bond of interest is usually lost in the background of competing bond responses. We show that strategic choice of incidence angle and input/output polarization combination enables a desired single-bond RA-SHG fingerprint response to "stand out from the crowd". We demonstrate the method by monitoring atomic-hydrogen etching of step rebonds at 600K, and bonding of cyclopentene (C_5H_8) to terrace dimers via 2+2 cyclo-addition.

RA-SHG bond fingerprinting



$$\vec{p}_j^{(2\omega)} = \beta_j^{||}\, \hat{b}_j\, (\hat{b}_j\, \hat{E}_{in}^{\omega})^2$$

$\beta_j^{||}$ = axial hyperpolarizability

$\hat{b}_j$ = bond unit vector

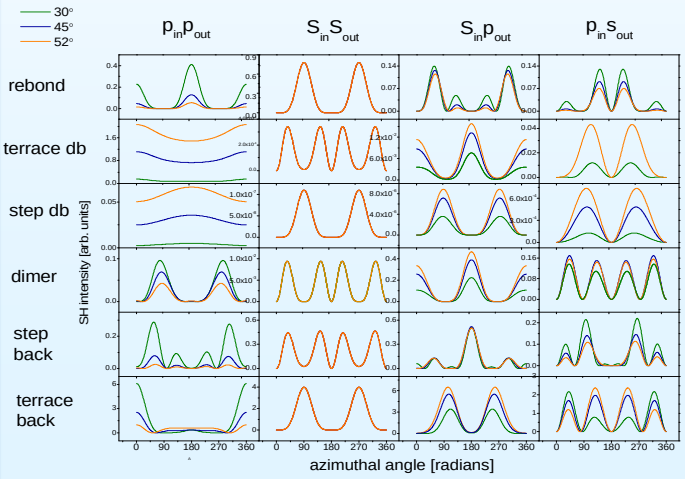
ab-initio DFT calculation provides input structure for SBHM analysis

Powell et al., Phys. Rev. B **65**, 205320 (2002)

$$\vec{E}^{(2\omega)} = \frac{e^{-ikr}}{r^2}(\vec{I} - \hat{k}\,\hat{k}) \sum \vec{p}_j^{(2\omega)}$$

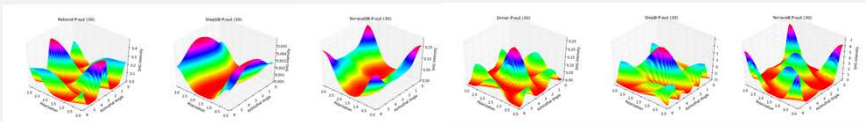
$$\vec{E}_j^{(2\omega)} = \frac{e^{-ikr}}{r^2}(\vec{I} - \hat{k}\,\hat{k})\ \vec{p}_j^{(2\omega)}$$

Dictionary of rotational anisotropies of individual bond responses



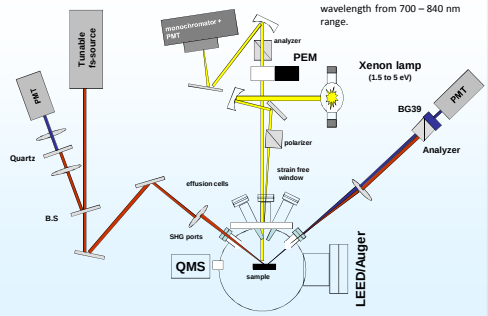
Exploring the parameter space

Using SBHM we calculate the SH intensity over all the parameter space



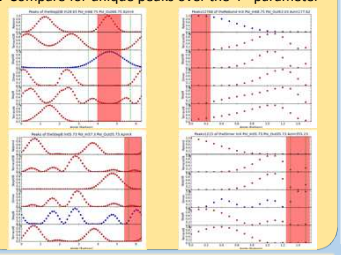
Experimental Setup

- Coherent MIRA Ti:Sapphire oscillator operated at a single wavelength from 700 – 840 nm range.



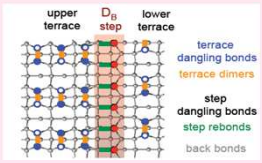
Geometrical "Fingerprinting"

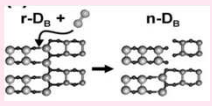
- From the predictions for SHG above we can systematically search for unique bond signals
- Choose a set of 3 parameters
- Normalize each set of signal by itself
- Compare for unique peaks over the 4th parameter



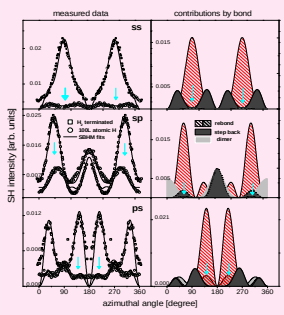
Breaking of rebonded r-D_B steps on vicinal Si(001)

- **Step rebond isolated at p-in/p-out 180° azimuthal angle**
- **Breaking of rebonded D_B steps by atomic H should affect this feature**



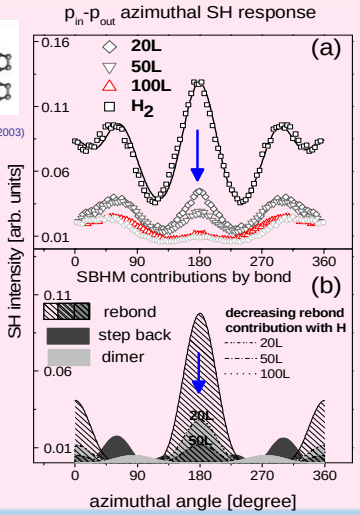


Laracuente & Whitman, Surf. Sci.**545**, 70 (2003)



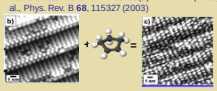
Surface preparation

- 10^6 L H_2 (saturation dose) passivates step AND terrace dangling bonds leaving terrace dimer and step geometry intact
- atomic H with sample at 300°C does not break terrace dimers.

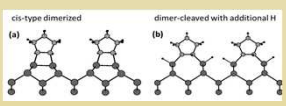


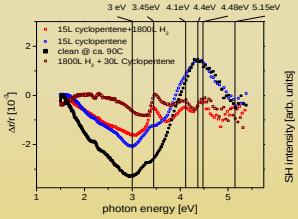
Self-assembled growth of cyclopentene on vicinal Si(001)

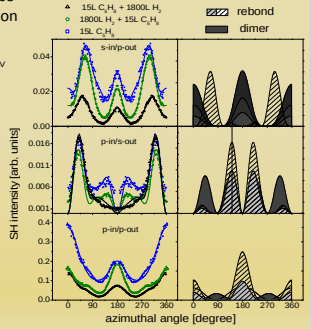
Hamers et al. Ac. Chem. Res. **33**(9): 617-624. (2000) Lu et al., Phys. Rev. B **68**, 115327 (2003)



- Ordered prototypical organic-silicon interface
- Self-assembled growth via [2+2] cycloaddition
- SHG and RAS used to monitor adsorption







- Hydrogen coadsorption allows to control adsoption structure from dimerized to dimer cleaved
- **SH-MAP bond fingerprinting** is able to monitor those changes
- Clarify adsorption at chemically active D_B steps

Conclusions

- ✓ **isolate individual bonds and track changes by surface chemical reactions**
- ✓ **simple experimental setup**
- ✓ **single wavelength fs-oscillator**
- ✓ **avoids multiparameter fitting**
- ✓ **applicable to many surface/adsorbate systems**

Acknowledgements

Robert Welch Foundation, NSF