

# COMPUTATION OF THE LOCAL ELECTRONIC DENSITY OF STATES FOR ALL SURFACE ATOMS IN DIFFERENT MICROFACET MODELS OF $TiO_2(100)1 \times 3$

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## ABSTRACT

Recently microfacets on reconstructed  $TiO_2(100)1 \times 3$  have been observed with atomic resolution by scanning tunneling microscopy (Murray *et al.* 1994) and surface core-level-shift photoelectron diffraction (Hardman *et al.* 1993). Determination of the electronic structure of extended surface defects is a formidable computational problem and only now possible by using the most powerful computers.

Earlier studies, by one of the authors (Michalewicz 1994a, 1994b, Michalewicz and Priebatsch 1995), on the electronic structure of transition metal oxides with high concentration of *point defects* in a very large atomistic models of up to 500,000 atoms, have now been extended to the very large samples with *extended surface defects* such as microfacets.

We present computed results for the Local Density of States (LDOS) for up to 13 nonequivalent Ti and O surface atoms in the vicinity of a microfacet, for five different models of a microfacet. This type of calculation might be useful for extracting information on atomic composition in the spectroscopic mode of operation of the Scanning Tunneling Microscope.

We also present the results of benchmark analysis of our electronic structure code on a vector-parallel computer (Cray C90). We compare vector-parallel performance with the SIMD performance (MasPar MP-1, MP-2 16K PE) and report on our efforts to implement the code on MIMD architecture (Cray T3D).

## I. INTRODUCTION

During the last four years a number of refined experimental studies of the rutile  $TiO_2(100)$  surface have appeared in the literature (Muryn *et al.*, 1991; Clark and Kesmodel, 1992; Zschack *et al.*, 1992; Murray *et al.*, 1994; Hardman *et al.*, 1993). With sophisticated experimental methods such as STM, glancing angle X-ray diffraction and LEED, the researchers were able to observe surface reconstruction and the appearance of  $TiO_2(100)1 \times 3$  microfacets. The surface electronic valence-band structure of  $TiO_2(100)$  and (110) faces was studied recently using angle-resolved photoemission by Hardman *et al.* (1994). It is hoped that by understanding the atomic and electronic structure of rutile surface, and especially the effects of surface steps and microfacets, the mechanism of photocatalytic decomposition of water observed by Fujisima and Honda in 1972 could be better understood (Muryn *et al.*, 1991).

While experiments give more new insights into the complex structure of surfaces, there has been rather slow progress in theoretical description of such systems. The electronic structure of rutile surfaces, both ideal and containing point defects was studied by Munnix and Schmeits (1984a, 1984b, 1985-1986).

The theoretical description of non-periodic structures poses formidable difficulties. When periodicity of infinite solid is lost one can no longer resort to simplifications offered by the Bloch Theorem and usually computations need to be done in direct space. Further, if large scale corrugations on the surface are to be included, the methods applicable for clusters or simpler atomic steps could prove to be (still) limited. Yang *et al.*, (1994) computed the electronic structure for a stepped Cu(110) surface using the recursive Green function method. Their sample was constructed from a supercell consisting of 150 atoms distributed over 5 layers and 25 chains. The electronic structure was computed for four atoms adjusting to the square angle atomic step.

An interesting computationally feasible alternative, based on the recursion method and the augmented-space formalism was recently proposed by Saha *et al.*, (1994). It still needs to be proven if it can be applied to realistic systems since, as authors note: "In spite of its immense potential the method could not be used for practical calculations because of the large dimension of the augmented space" (Saha *et al.*, 1994). It was exciting to see that *ab initio* method of Car-Parrinello was successfully applied to study dissociation of water at a stepped *MgO* surface (Langel and Parrinello, 1994). These computations showed that in contrast to the perfect surface, dissociation of water proceeds very rapidly at the stepped surface.

In the present work we use the equation of motion method (EoM) (Alben *et al.* 1975; Beeman and Alben 1977) to compute the local electronic densities of states for up to thirteen outermost nonequivalent *Ti* and *O* atoms in the vicinity of a microfacet. Five different microfacet models of reconstructed  $TiO_2(100)1 \times 3$  surface which we studied will be described in the next section. The equation of motion method was described in detail in a number of previous publications; *e.g.* see (Michalewicz, 1994b) for further references.

## II. MODELS OF MICROFACETS ON $TiO_2(100)1 \times 3$

The crystallographic structure of ideal rutile  $TiO_2$  (Grant, 1959; Howard *et al.*, 1991) and its most stable surfaces (110) and (100) (Henrich and Cox, 1993) is well known. The tetragonal unit cell consists of two *Ti* and four *O* atoms. The titanium atoms occupy the positions  $(0, 0, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  whereas oxygens are at the positions  $\pm(x, x, 0)$ , and  $\pm(\frac{r}{2} + x, \frac{1}{2} - x, \frac{1}{2})$ , where  $x = 0.306 \pm 0.001$  (Grant 1959).

Based on data derived from LEED symmetry and photoemission spectra Muryn *et al.* (1991) proposed the missing row model (MR) for the reconstructed  $TiO_2(100)$  surface (Figure 1).

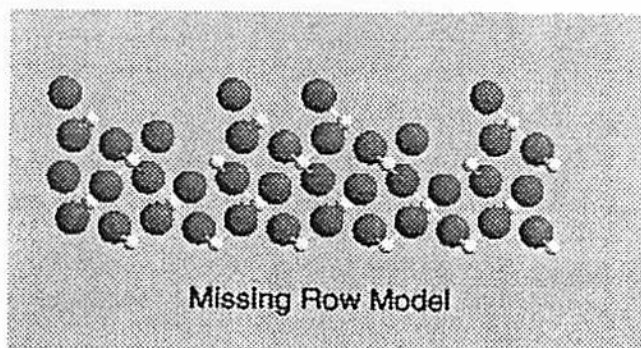


FIG. 1. Missing row model of  $TiO_2(100)1 \times 3$  projected on (001) plane.

Soon after, Zschack *et al.* (1992) found that the microfacet model (MM) (Figure 2) was in better agreement with glancing angle X-ray diffraction and LEED measurements than the missing row model.

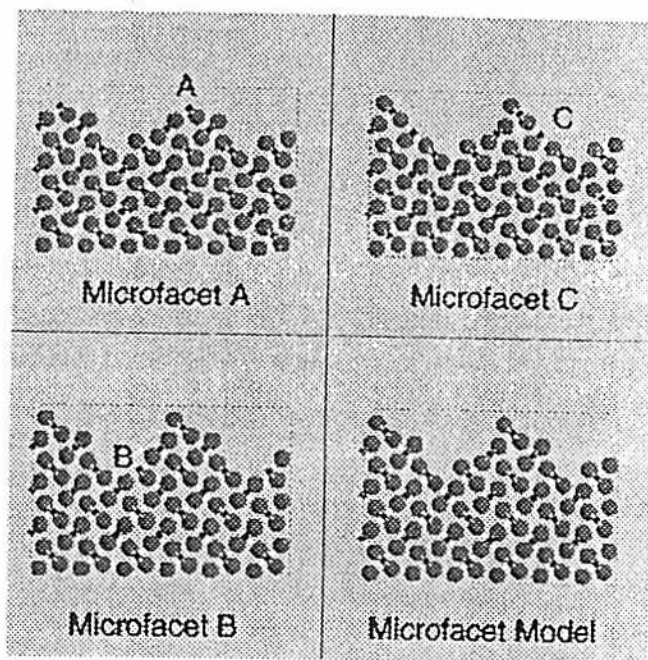


FIG. 2. Four different realisations of microfacet model; three with ordered arrays of oxygen vacancies (A, B and C) and the microfacet model with no rows of oxygen vacancies (MM) viewed along the [001] direction (after Hardman *et al.*, 1993)

We used all five models: missing row (MR), microfacet model (MM) and microfacet models A, B and C (MMA, MMB and MMC respectively) to study the effect of the local environment on the local electronic density of states (LDOS). This type of information is especially useful when analysing Scanning Tunneling Microscopy (STM) images. STM images of reconstructed and reduced surfaces of  $TiO_2(100)1 \times 3$  were obtained by a number of groups (Clark and Kesmodel, 1992; Hardman *et al.*, 1993). In all studies the images are obtained at positive sample bias, *i.e.* the electrons tunnel from the tip into unoccupied *Ti* 3d states. It was reported that the images at negative tip bias could not be obtained. This means that the STM probe the location of the *Ti* atoms and can not distinguish between different reduced surface models (MMA, MMB or MMC). The results of our calculations which we present in the following section attempt to answer the question: which model is physically realised?

Figure 3 represents the state-of-the-art STM image of  $TiO_2(100)1 \times 3$  surface.

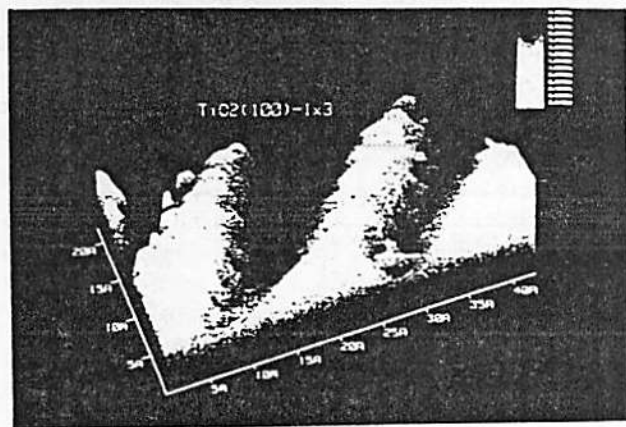


FIG. 3. A constant current image of the vicinal  $TiO_2(100)1 \times 3$  surface (+2V, 0.3nA). The image, in which the rows lie parallel to the [001] direction, is displayed as a tilted, three-dimensional figure for case of viewing (from Murray *et al.*, 1991).

### III. LOCAL DENSITY OF STATES

The massively parallel implementation of the equation-of-motion program designed for array processor SIMD architecture (Michalewicz, 1994b) was modified specifically for MIMD (as well as SIMD) machines. The sample can now be rotated, arbitrary crystallographic faces can be exposed and the extended surface defects such as steps, islands and microfacets can easily be built as software masks. The local electronic density of states for up to thirteen nonequivalent atoms on the surface of microfacet for five models of microfacet (MR, MM, MMA, MMB and MMC) were computed using the new version of our program. The full results will be published elsewhere. Here we present the characteristic results for the Microfacet Model at positions indicated in Figure 4.

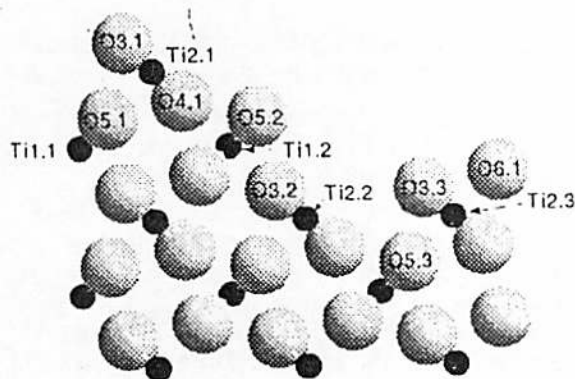


FIG. 4. Five Ti (small black circles) and eight O (large circles) atom sites at which the LDOS was computed.

The results are presented in Figure 5. The LDOS for all four models derived from Microfacet Model are very similar. One striking feature is complete lack of covalent mixing and narrow  $s$  and  $p$  bands at oxygen site O5.2. This feature is present in all three models (M, M, MMC and MMB). This indicates lack of bonding of O5.2 atom at microfacet. It would mean that Microfacet Model C is the most likely to represent the reduced reconstructed  $TiO_2(100)1 \times 3$  surface. This result is different from the conclusions of Hardman *et al.*, 1993. Based on time-reversed dynamical LEED formalism those authors suggest that Microfacet Model A is the one which gives the closest agreement with their LEED experimental data. We need to investigate the arguments based on the local symmetry at each sites (A,B and C) in order to confirm our finding.

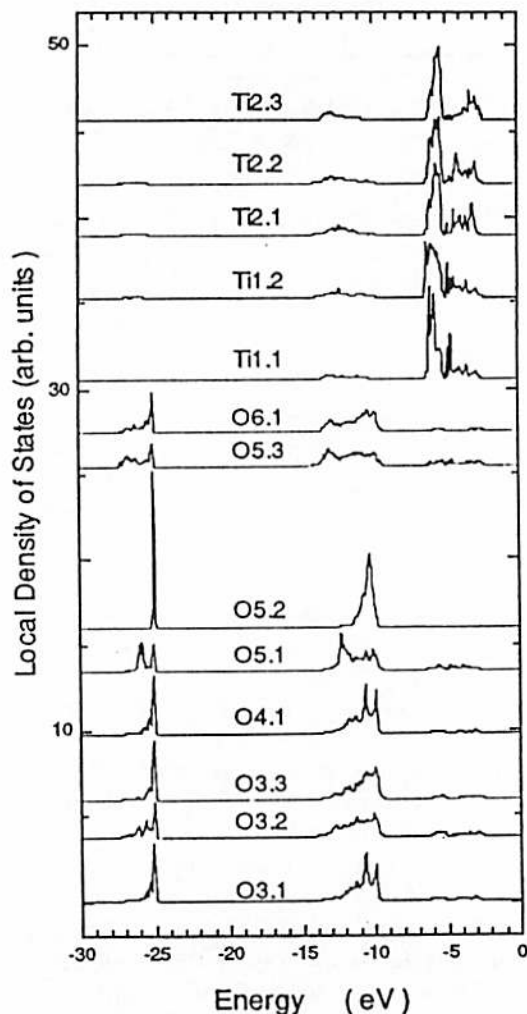


FIG. 5. The Local Electronic Density of States for surface atoms in Microfacet Model (MM) at positions indicated in Figure 4. Note complete lack of covalent mixing and spread of bands at site O5.2.

#### IV. BENCHMARKS

The production code was run on the CRAY C9016E/16256-4 vector-parallel machine with 16 processors, 256 Mwords memory and having 4.167 nanosecond clock. This is the third version of the code. This one ran nearly ten times faster on a single processor C90, than the first vectorized version on Cray 2 (Michalewicz *et al.*, 1992). The size of the system had to be large enough to enable efficient vectorization. Depending on the size of the sample the program ran between 550 to 630 MFlop/s on a single processor C90. This means we achieved about 55% to 63% efficiency of a single vector processor of CRAY C90. The sample sizes in  $x, y$  and  $z$  dimensions were  $6 \times 6 \times 6$  (1296),  $10 \times 10 \times 12$  (7200)  $12 \times 12 \times 12$  (10368),  $16 \times 16 \times 16$  (21574) and  $18 \times 18 \times 18$  (34992) unit cells (atoms). Each unit cell contained six atoms. The results of benchmarks are given in Figures 6 and 7.

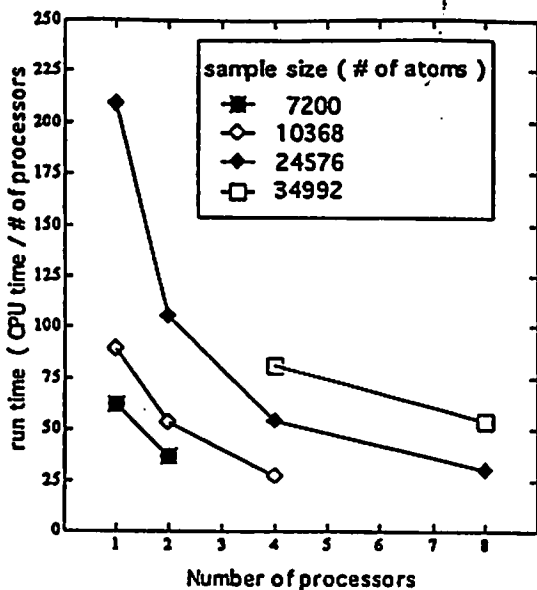


FIG. 6. Running time for systems of four different sizes vs. number of processors of 16 processor CRAY C90.

The running time was defined as the total CPU time divided by the number of processors which ran a particular job. The running time defined this way differs slightly (up to about 15%) from the wallclock figures given on completion of each job. The discrepancy is attributed to the fact that we run our program on a busy machine with many jobs competing for the resources. For a given sample size the slope of each curve decreases with the number of processors. This indicates deterioration of performance of each processor as the number of processors used grows. The best performance achieved was 4.43 GFlops when we run our code on 8 processors (wallclock 33s, system size 24576 atoms). Unfortunately we were not able to improve this performance by increasing

<sup>of</sup>  
~~the number of processors above eight. When we ran the code on 16 processors, the performance on each processor deteriorated to only about 281 MFlops/s per processor. The wallclock was again 34.5s, and the total speed 4.4 GFlops/s, however the total CPU time was nearly double that for eight processors.~~

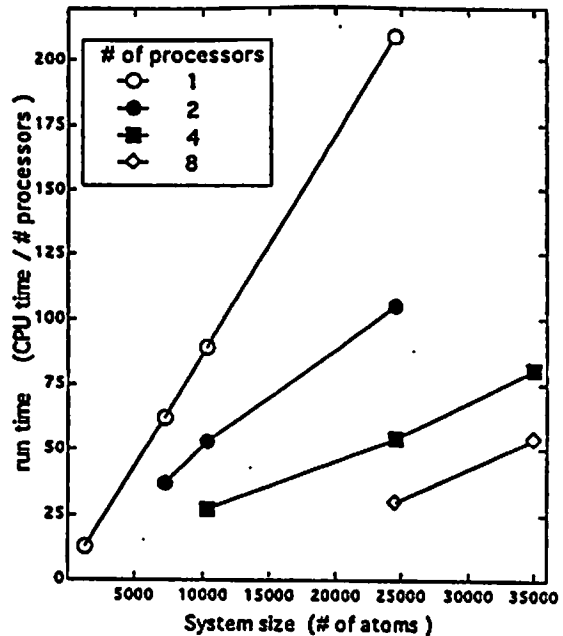


FIG. 7. Running time as the function of the system size for different numbers of processors employed.

Figure 7 shows that the computational complexity of the vector-parallel version of the equation of motion program is linear with the size of the sample. The slope grows smaller when larger number of processors is employed. It is interesting to compare this with "perfect" scaling achieved on SIMD MasPar machine (Michalewicz and Priebatsch, 1995). SIMD architecture had a number of very appealing features. It was easier to visualize mapping physical dimensions onto the dimensions of array of processors. The programming model was easier. It was simple to scale up the size of the system in  $x$  and  $y$  dimensions. However, the scaling in  $z$  dimension was not "perfect", but linear and the small local memory on each processor limited the thickness of sample in a serious way. The high performance on the SIMD machine was achieved by enlarging the system size up to the limits enforced by the available memory resources. This way it was possible to run the program for nearly 500,000 atoms on 16K processors of MasPar with 1Gbytes memory. We managed to achieve the speed of 740 MFlops/s on MasPar MP-2216 (Michalewicz and Priebatsch, 1995). In the present work we achieve similar speed on a single processor CRAY C-90 for systems of smaller sizes.

## V. CONCLUSIONS

There is a need for very fast and efficient codes to calculate the electronic structure of novel complex materials. Defects engineering might lead to exciting new materials and devices. The equation-of-motion method, as implemented in this work, can be used to study disordered transition metal oxides, amorphous semiconductors, the electronic structure of random point and extended defects and their influence on the electronic properties of materials.

With the program reported in this work we studied the local electronic structure of *Ti* and *O* atoms in the vicinity of  $TiO_2(100)1 \times 3$  microfacets. The samples were up to 35992 atoms in size. The wallclock time for the sample of 21576 atoms for all thirteen atoms (each atom requires new initialization) takes about 730 seconds (286-Is CPU) on four processors of sixteen processor CRAY C90. The peak speed achieved in benchmarks was 1.1 GFlops/s.

We are working on the massively parallel MIMD implementation of this program on Cray T3D machine. The current version of the program, developed specifically for MIMD architecture scales identically in all three spatial dimensions of a sample. It is possible to manipulate a sample, rotate it, study various crystallographic faces and extended surface defects.

In the near future we plan to extend the reported work to study  $TiO_2(110)$  surfaces without and with defects.

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## REFERENCES

- Alben, R.; Blume M.; Krakauer, H. and Schwartz, L. 1975. *Physical Review B* 12, 4090
- Beeman D. and Alben, R. 1977. *Advances in Physics*, 26 339
- Clark, G.W. and Kesmodel, L.L. 1992. *Ultramicroscopy* 41, 77-81
- Fujishima, A. and Honda, K. 1972. *Nature* 238, 37
- Grant, F.A. 1959. *Reviews of Modern Physics* 31, 646
- Hardman, P.J.; Prakash, N.S.; Muryn, C.A.; Raikar, G.N.; Thomas, A.G.; Prime, A.F.; Thornton, G. and Blake, R.J. 1993. *Physical Review B* 47, 16056
- Hardman, P.J.; Raikar, G.N.; Muryn, C.A.; van der Laan, G.; Wincott, P.L.; Thornton, G.; Bullett, D.W. and Dale, P.A.D.M.A. 1994. *Physical Review B* 49, 7170-7177
- Henrich, V.E. and Cox, P.A. 1993. *The Surface Science of Metal Oxides*. Cambridge University Press, Cambridge
- Henrich, V.E.; Dresselhaus, G. and Zeiger, H.J. 1976. *Physical Review Letters* 36, 1335-1338
- Howard, C.J.; Sabine, T.M. and Dickson, F. 1991. *Acta Crystallographica B* 47, 462-468
- Langel, W. and Parinello, M. 1991. *Physical Review Letters* 73, 504-507
- Michalewicz, M.T.; Shore, H.B.; Tit, N. and Halley, J.W. 1992. *Computer Physics Communication* 71 222
- Michalewicz, M.T. 1991a. "Massively Parallel Studies of the Electronic Structure of Disordered Micro-crystallites of Transition Metal Oxides." In *High Performance Computing 1994*, Proceedings of The Society for Computer Simulation Multiconference (San Diego, CA, Apr.10-15). A. Tentner, Ed., The Society for Computer Simulation, San Diego, 1994, 108-113;
- Michalewicz, M.T. 1994b. *Computer Physics Communications* 79, 13-23
- Michalewicz, M.T. and Priebsatsch, M. 1995. *Parallel Computing* (in press)
- Munnix, S. and Schmeits, M. 1981a. *Physical Review B* 30, 2202-2211
- Munnix, S. and Schmeits, M. 1981b. *Solid State Communications* 50, 1087-1089
- Munnix, S. and Schmeits, M. 1985. *Physical Review B* 31, 3369-3371
- Munnix, S. and Schmeits, M. 1986. *Physical Review B* 33, 4136-4144
- Murray, P.M.; Leible, F.M.; Muryn, C.A.; Fisher, H.J.; Flipse, C.F.J. and Thornton, G. 1994. *Physical Review Letters* 72, 689
- Muryn, C.A.; Hardman, P.J.; Crouch, J.J.; Raikar, G.N.; Thornton, G. and Law, D.S.-L. 1991. *Surface Science* 251/252, 747-752
- Prabhakaran, K.; Purdie, D.; Casanova, R.; Muryn, C.A.; Hardman, P.J.; Wincott, P.L. and Thornton, G. 1992. *Physical Review B* 45, 6969-6972
- Saha, T.; Dasgupta, I. and Mookerjee, A. 1994. *Journal of Physics: Condensed Matter* 6, L245-L251

Yang, C.-K.; Cheng, Y.-C. and Wu, S.Y. 1994. *Physics Letters A* 188, 68-72

Zschack, P.; Cohen, J.B. and Chung, Y.W. 1992. *Surface Science* 262, 395-408

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