Atomic scale simulations of dopant adsorption on low index Ni crystal surfaces

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This report summarizes the plan of work for the next 4 months

A. Background:

Over the summer of 2011, Ms. Yin, a new graduate student at Lehigh who is supported via the MURI project, began training in using atomic scale resolution computational simulations. Ms. Yin's Ph. D. research will combine computational studies with transmission electron microscopy experiments to better understand fundamental mechanisms of formation and stability for complexion phases. Computational efforts so far have focused on molecular dynamics (MD) techniques; Monte Carlo (MC) techniques will be employed in a future stage of the project. The former methods will be used to compute dynamic properties, such as dopant diffusion, while the latter methods will be used to explore equilibrium structures of dopants on free surfaces and at grain boundaries. This research benefits from the use of pre-existing codes; in the case of MD, a massively parallel, open source code (LAMMPS) is used. For MC calculations, an in-house code will be used; this code, developed by PIs Rickman and Webb in a separate research effort, is capable of implementing different types of atomic ensemble manipulations (trial moves). Research between Webb and Yin has so far been of a development nature; as such, this monthly report will summarize the research plan being executed, which will be reported upon in subsequent monthly updates.

B. Stage 1 Research Plan:

This component of theoretical research will focus on metal systems, with <u>Ni</u>-Bi being the canonical system (note, in the prior notation, the host material is underlined). Prior work by MURI team participants observed bilayer interfacial phases (i.e complexions) of Bi at all random grain boundaries examined in Ni host samples. From prior results, a thermodynamic model was developed to describe the formation and stability of the complexion phases. The work summarized here will attempt to augment this thermodynamic model by using atomic simulations to directly evaluate mechanisms of dopant phase formation on low index Ni free surfaces.

The general idea of the pre-existing thermodynamic model is that, to first order, adsorption sites at a grain boundary can be interpreted in terms of the collective ensemble of adsorption sites on the two free crystal surfaces forming the given boundary. Even for a free surface, identifying adsorption sites, particularly in the presence of multiple adsorbent atoms (adatoms), can be non-trivial. This is because a significant size mismatch exists between Ni and Bi (note, this is also true of <u>Cu</u> and Bi, another system being explored in the MURI project because evidence of complexion behavior has been observed). Because Bi atoms are ~40% larger than Ni atoms, they cannot occupy every position on the surface that would normally be occupied if an additional plane of Ni atoms was added to the surface; this is because repulsion between neighboring Bi atoms would be too high. This frustration leads to interesting surface adsorption behavior. Furthermore, when two randomly rotated (i.e. twisted) surfaces are brought together –

even of the same index – how adsorption sites combine is unknown. Lastly, since complexion phases are observed to form at high temperatures, differing thermal expansions of constituent phases further complicates details of adsorption. These issues are fundamental to the previously developed thermodynamic model and atomic scale simulations will explore them in a direct fashion.

Currently, a literature summary of free surface adsorption studies for similar binary systems is being assembled. For instance, a number of LEEM studies of Pb sub-monolayer adsorption on Cu have revealed non-trivial free surface behavior; note the size mismatch in the Pb-Cu system is similar to the mismatch for Ni-Bi and Cu-Bi. Thus, relevant free surface literature is being summarized to properly couch our calculations. Simulation research is currently focused on formation of low index free surfaces – (001), (110), and (111) – of Ni and equilibrating such surfaces at temperatures relevant to complexion phase formation. For equilibrated surfaces, a single atom adsorption site algorithm (under development) will reveal the structure of adsorption sites in the limit of a single adatom. This baseline description of adsorption sites, though influenced by the aforementioned size mismatch, is expected to adopt a relatively straightforward periodicity related to the underlying Ni lattice sites. Calculations will test this assumption. Following this, adsorption structures will be explored for increasing concentration of adatoms, with the goal of elucidating the fully covered surface structure. The final step of this stage of research will be to form the analogous grain boundary and evaluate adsorption at this boundary. In this way, the research will be poised to directly reveal the combining rules that lead from a set of free surface adsorption sites to an analogous set of grain boundary adsorption sites.

While the size ratio of Bi and Ni is well established, the relevant interaction potential is not. This is not true for the pure Ni system: our research is already employing a well-verified embedded atom method potential for Ni. In the absence of a pre-existing potential to describe Ni-Bi and Bi-Bi interactions, companion research efforts under the MURI project will explore interaction optimization via quantum mechanical calculations. Such calculations will not be described in detail here but, in summary, quantum mechanical level descriptions of cluster energy for NiBi clusters, as well as forces between atoms within a cluster, will be used to optimize an interaction potential suitable for classical level atomic scale calculations. While quantum level simulation research progresses, the effort described herein will proceed in parallel with an approximate interaction potential. In the approximate model, the constituent atoms' atomic radii (i.e. for Ni-Bi) will dictate length scale parameters in the potential; furthermore, the interaction strength of the Bi-Bi potential will be dictated by the ratio of the Bi melting point to the Ni melting point. Lastly, the Ni-Bi interaction will be varied, in order to understand how adsorption site distributions depend upon the strength of interaction between dopant and substrate. Treating the strength of interaction between adatom and substrate as a variable will broaden the impact of the results by generalizing observed behavior. Lastly, in order to employ a fully pre-existing and verified interaction potential, we are now initiating parallel studies in the Pb-Cu system, for which such a potential has been published. This will further broaden the applicability of obtained results.