

# Structural investigation of bimetallic and high Miller index surfaces using low energy electron diffraction

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## 論 文 内 容 の 要 旨

### Thesis Summary

The main purpose of the research presented in this thesis is to comprehend the structural parameters of bimetallic surfaces by optimizing the experimental conditions. The bimetallic surfaces can be defined as the less than monolayer of ad-metal deposited on a single crystal metal substrate. By optimizing the adsorption condition, the bimetallic surface can be tuned for the adsorbate to form either of substitutional alloy, subsurface monolayer or overlayer structure. On the other hand, the surface structure of high Miller index clean single crystal substrates itself can be very intriguing as it undergoes surface relaxation and reconstruction due to lower coordination number of surface atoms. In this thesis the experiments were carried with quantitative low energy electron diffraction and inside the ultra-high vacuum chamber. The structural determination of all these kinds of substrate can be the stepping stone towards elucidating the nature of the surface, hence its properties.

The research work presented in this thesis explores the structural parameters of two dimensional honeycomb structure of Group IV metal, tin and lead which is termed as stanene and plumbene respectively. All the structural analysis was carried out using quantitative low energy electron diffraction (LEED). First, I checked all models limited to symmetry  $p3m1$  having Sn coverage between 0.25 to 0.75 with adsorption up to two surface layers for the Cu(111)- $p(2 \times 2)$ -Sn structure and firmly confirmed the overlayer honeycomb structure, which can be described as a 2D sheet of stanene having the lowest Pendry R factor. The structure is further optimized to obtain an Rp factor as low as 0.14. A detailed calculation is carried out in this research, which conclusively shows the lateral and vertical displacements for each atom in three sub-surface Cu layers. From the structural analysis the stanene structure is realized to exhibit with zero buckling. It is demonstrated that the underlying Cu atoms played an important role in stabilizing the ultra-flat honeycomb structure. the Sn-adsorbed Cu(111) surface shows the opposite sequence of relaxation compared to the clean Cu(111) surface, expansion between the first two layers and compression between the subsequent layer which is expected to arise to stabilize stanene, allowing an ultra-flat 2D structure to be realized.

Whereas the plumbene structure was confirmed on Pd(111) surface after annealing the Pb deposited substrate at 600 °C to form  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. Interestingly, beside the plumbene structure at coverage 2/3, another Pb-Pd alloy structure at coverage 1/3 forming bimetallic surface alloy was also determined using LEED. The detail structural analysis of both the structures are presented in this thesis. When annealed at above 600 °C, the one Pb atom substitutional alloy per unit cell structure

has the lowest Rp factor with very small bond length between the Pb-Pd atom. However, when the annealing temperature is lowered to 350 °C we obtain smallest Rp factor for two different structures specially by excluding the mirror plane in our analysis. One of the structures is the honeycomb plumbene structure and the other is the substitutional alloy structure that I obtained at high temperature annealing condition. However the structural and non structural parameters of the same structure is different at different annealing conditions. The detail structural analysis and comparison is presented in this thesis. The honeycomb plumbene alloy structure undergoes buckling and is stabilized by the lateral displacement of the second layer Pd atoms. The buckling is comparable to the previous theoretical and experimental results.

To interpret the crystal growth and reaction kinetics of adsorbates in “real” surface which is used industrially having various kinds of defects or crystal orientation, the structural analysis of high Miller index Cu(410) surface is discussed here. The surface atoms of Cu(410) undergoes considerable interlayer relaxation due to the low coordination number of surface atoms having unit cell which consists of terrace of four atoms followed by step of one atom. The optimized interlayer relaxation sequence can give important information about the site selection of adsorbates. The QLEED-determined Cu(410) structure exhibits alternating sequences of expansion (+) and contraction (-) (of the first 16 atomic interlayers) relative to the bulk-truncated interlayer spacing of ca. 0.437 Å, with a Pendry reliability factor  $RP \approx 0.0797$ . The corresponding electron distribution shows smoothening relative to the bulk-determined structure. Thus, we demonstrate how high Miller index surface, viz., Cu(410), can serve as an intermediate stage for analyzing and understanding the role of defects on the atomically flat surface, e.g., how they change their physical and chemical properties, how adsorbates behave near surface defects, and the adsorption mechanism. This detailed interlayer relaxation (including the perpendicular and lateral displacements of the surface atoms) of high Miller index Cu(410) may also yield a better understanding of the merits and limitations of widely used experimental and theoretical methods for surface structural analyses. In order to interpret the interaction of Si with Cu atoms where Si is often used in industrial reaction with Cu as the catalyst, the adsorption of Si on Cu(410) is investigated and p(2X2) structure is found. From the analysis among several possible structural models, a most probable structure is proposed in this thesis. The structural information will further help to optimize the reaction kinetics. The thesis also presents several prospects of future research that can be carried out including adsorption of different heavy metals such as Sn, Bi on Pd(111) surface giving different new structures.

The thesis also contains two Appendix where I have shown the research work carried out at the National Institute of Nanotechnology in Alberta, Canada as part of my international internship program. In that studies I have carried out the experiment on understanding the atomic transitions on tungsten tips used in electron microscopes. All the research topics, although little diversified but in general context are interrelated and serve to satisfy the motivation of this thesis.