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Surface Relaxation of Clean Mo (110), Optimization of Sn Adsorption and Ab-Initio Calculation of The Electronic Density of States (DoS)

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Abstract: *Herein we report the multilayered atomic model of Mo(110) analyzed by low energy electron diffraction (LEED) and consequent determination of the density of states (DoS) by density functional theory calculations. The surface relaxation of the atomic layers has been investigated for the adsorption of Sn. Different Sn structures depending on the coverage and conditions has been confirmed by LEED. It is evident from our experiment that, in order to compensate the contraction between 1st and 2nd atomic inter layers, the atomic inter-layer spacings between the 2nd and 3rd and between the 3rd and 4th inter atomic layers are found to be increased.*

Keywords: Mo(110), Sn, LEED, structural model, DoS.

1. INTRODUCTION

Determination of the atomic structure and associated properties of any surface gives an easy and lucid understanding with regards to the applicability of the surface for adsorption, growth and deposition process which involves complex phenomena. Over the years, it always has been a subject of interest among the researchers.

Molybdenum (Mo) as a transition element is thermally stable in comparison to other commercially used counterparts [1,2]. As a result, it is preferred as a substrate to investigate surface adsorption kinetics for different elements. Mo(110) surface has been earlier specifically examined by Gafner [3] but it did not include the computational refinement process. Later, Garza and Clarke [4] also investigated the Mo(110) surface where non-structural parameters have also been considered including Debye temperature formulated by “Zanazzi and Jona R-factor” method [5]. It is observed in several instances that systemic errors are likely to exist due to the complexity of computational statistics which require to be reviewed and refined with simple computational methods. Simpler computational technique based on structural choice of sites for adsorption along with non-structural parameters can minimize the discrepancies in estimation of lattice sites. Apart from computational refinement technique, structure investigation with extended energy range is also required. Hossain et.al. earlier investigated the multilayer surface relaxation of W(110) using similar methodology to investigate adsorption of B [6].

Adsorption of Sn on different surfaces congregated interest after the discovery of localized superconductivity in Sn films. The insulating layers has been found to be evolved to localized metallic superconductivity with increase in thickness and subsequent decrease in sheet resistance [7]. Experimental realization of “stanene” has also been successful in the year 2015 [8] which stimulated further investigation for plethora of properties such as enhanced thermoelectric performance, topological superconductivity and the near-room-temperature quantum anomalous Hall effect. Tikhov and Bauer found several Sn structures and unusually strong electronic interactions in the Sn-Mo systems which require further investigations [9]. Some more works had also been done for Sn adsorption on Mo(110). For example, Krupski observed layer-by-layer growth (Frank-van der Merwe mode) while depositing Sn layers on Mo(110) [10]. Maehara et.al. also investigated the growth behavior and observed various Sn structures by reflection high-energy electron diffraction (RHEED) analysis technique [11]. Apart from the formation of Mo_3Sn which is an intermetallic compound, only at very high temperatures (>1000°C), occurrence of any other chemical reaction is not found to be feasible [10]. Not only Sn, but also SnO_2 is a material of technological importance as it has application in the areas of gas sensing, catalytic surfaces, transparent electrodes etc. [12].

Low energy electron diffraction (LEED) analysis is a very reliable and established technique to determine the atomic geometry of crystalline surfaces with precision. The experimental LEED intensity data w.r.t energy variation are compared with several optional/trial atomic structural models with consideration of thermal vibrations and various other factors which effect the intensity. Among the several trial atomic structural models, one model will seem to agree with experimental pattern evaluated by the reliability factor i.e. R-Factor. The R-Factor of the agreeing model will be the lowest by a fair margin in comparison to the other models which will then be further refined. Therefore, we have used LEED technique to find the surface relaxation of clean Mo(110) and other surface structure of Sn adsorption.

As the adsorption and chemical bond between a surface and an adsorbate (atom or molecule) are a function of chemical reaction due to electronic states of the surface and the adsorbate species which is incident on the surface, it is always required to understand the electronic properties of surfaces as surface adsorption are sometimes tricky to understand due to variations of state of matter such as the interface between solid-solid, solid-liquid or solid-gas. Also, metals provide semi-infinite source of electrons at the fermi level due to its band structure as a result of which metals are conductors are good conductors of heat and electricity.

We have also analyzed the electronic density of states (DoS) using density functional theory (DFT) first principle simulations for the Mo(110) surface. The electronic density can explain electronic interactions between surface and adsorbate. Kawajiri et.al. earlier presented a one-dimensional density of states on Mo(110) [13]. Palotás et.al. earlier have calculated electronic characterizations of one monolayer Rh on Mo(110) surface by DFT calculations [14].

Herein we will discuss the details of the clean Mo(110) surface relaxations for p(1×1) structure and Sn adsorption on its surface. Our future endeavor will include the detailed analysis of the formed structures of Sn on this surface and we will try to prepare SnO_2 as well and check the LEED patterns.

In order to understand the adsorbate-surface interaction between Sn and Mo(110) surface, we've carefully tried to understand the relaxation of the interatomic layers. The few layers of atoms from surface is primarily responsible for the physical and chemical attributes, the surface has to offer. Also triggered by the fact that, inconsistencies always remain in the experimental findings about interlayer relaxations due to various factors such as new surfaces, possible discrepancies in experimental or theoretical findings, we decided to examine the surface in details before introducing Sn-flux on the surface.

2. EXPERIMENTAL PROCEDURE

The whole experiment has been accomplished under UHV conditions ($<6\times10^{-8}$ Pa) except the oxidation process. Apart from e-beam evaporator and LEED system, the vacuum deposition chamber also contains quartz crystal microbalance (QCM) to monitor the deposition flux. The surface was cleaned by repeated cycles of oxidation (at 1200 °C under O_2 pressure of $\sim5\times10^{-6}$ Pa) and flashing (1800 °C at $<6\times10^{-8}$ Pa). Oxidation of the surface has been accomplished at elevated temperatures to form multi crystallite MoO_2 followed by subsequent flashing at 1800 °C under UHV conditions. This was done for the removal of chemically bonded oxygen from the surface along with other impurities. The LEED pattern was recorded with the help of digital charge-coupled device (DCCD) camera integrated with digitally software aided data acquisition system as shown in the captured images as shown in Fig. 1 for the clean surface and Fig. 5 for Sn-superstructures. The variation of Intensity with energy of incident electron beam i.e. I(E) curves were generated after adjusting the orientation of the surface to get the symmetry-degenerate and conjugate patterns. The orientation requires to be properly adjusted by symmetrizing (same intensity) the symmetry-degenerate conjugate beams. The I(E) curves of the first order diffraction spots were taken into consideration followed by the second order diffraction spots. The conjugate beams which belong to the same family of planes were averaged for better precision.

Sn flux was generated by using an e-beam evaporator (Sn-source) under UHV conditions and incident (perpendicular) on cleaned Mo(110). Prior to deposition on Mo(110), the deposition rate due to Sn-flux was monitored using the QCM. Adsorption were attempted at different temperatures from room temperature up to 350 °C. The LEED patterns were taken for different conditions and acquisition time prior to the consideration

3. STRUCTURAL CALCULATION

In order to obtain the atomic sites and subsequently the structural model, we've used the symmetrized and automated tensor LEED package formulated by Barbieri/Van Hove [15]. This LEED procedure is similar to earlier proposed model by Zanazzi and Jona R-factor model but with simpler method to model the atoms.

Keeping the imaginary part of the inner potential (V_ω) fixed at -5.0 eV, we've determined the real part by fitting the theoretical calculation with the experimental data. Each model exhibits a unique Pendry reliable factor (R_p) [16]. The model is obtained by achieving the best fit (the lowest R_p value) among various models which stands out by a fair distance by agreement with the experimental data. The error bar in structural parameters was calculated by variance of R_p,

$$\Delta R = R_{min}(8|V_\omega|/\Delta E)^{1/2} \ldots\ldots\ldots\ldots\ldots(3.1)$$

where R_{min} is the lowest Rp value and ΔE is the total energy range of the experimental I(E) curves [16].

We have used the VESTA software package to depict the atomic model along with their positions. The adsorption of Sn on the Mo(110) surface will be later analyzed by similar procedure.

4. DENSITY FUNCTIONAL THEORY (DFT) CALCULATIONS.

We've used the ab initio (first principle) calculations using quantum espresso codes based on BURAI 1.3 software suite which is a graphical user interface (GUI) of Quantum Espresso based on Density functional theory (DFT) calculations [17, 18]. We've used "crystallographic input file" (.cif) as the input source for the required crystallographic parameters for the calculations. The .cif file as input for BURAI is extracted as output from VESTA (Ver. 3.5.7) software suite for the DFT calculations.

5. RESULTS & DISCUSSION

5.1 Analysis of the LEED pattern

We have obtained a clean Mo(110) surface at atomic scale by the cleaning procedure for generating the LEED pattern as shown in Fig. 1. The p(1×1) structure is also demonstrated by the red diamond in the Fig.1.

Initially the structure of the clean Mo(110) has been determined to the most possible precision by tensor LEED. For the clean Mo(110), six different conjugate spectra has been considered viz. {1,0}, {1,1}, {1,-1}, {2,0}, {2,-1}, {2,1}. The minimum Pendry R-factor (Rp) has been obtained by refining the model multiple times by the non-structural factors after the lattice sites are determined. The Debye temperature is an important non-structural parameter which also determines the Pendry R-factor and the lattice sites. Biaxial symmetry has been considered with symmetry planes along Z=0 and Y=0 respectively. The optimized Debye temperatures are 267 K for the first layer and 377 K for the other layers. Various structural parameters have been considered along with the reflection parameters. The fitting of the experimental curves is shown in the Fig. 2. The maximum range of data is 80-500 eV.

Based on this fitting, further analysis is continued which involves real space realization of the atoms, and consequent calculation of the electronic density of states (DoS). So, it is very important to precisely fit the theoretical model with the experimental data as much as possible in order to remove errors in further calculations based on the atomic model.

The calculations for interlayer relaxation will be followed based on the calculations and fitting of the model by iterations.

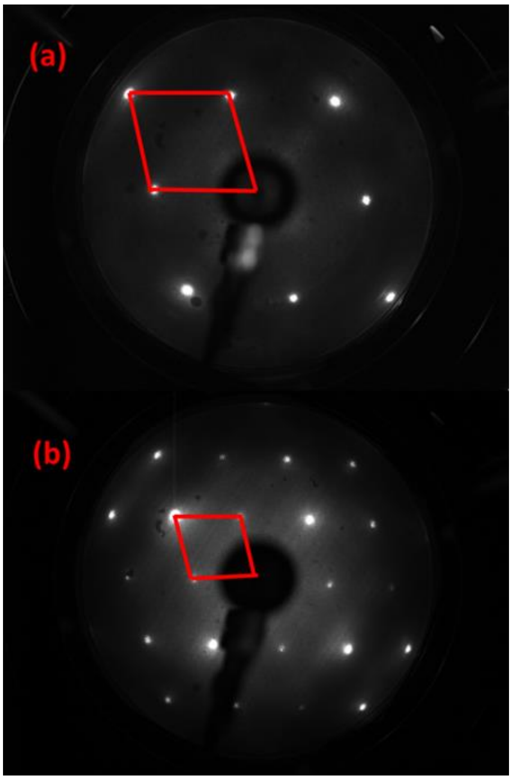

Fig. 1. Distinct LEED pattern of the (a) 1st order diffraction spots of clean Mo(110) at 125 eV (b) consideration of the diffraction spots at 300 eV. The unit cell is represented by the red diamonds.

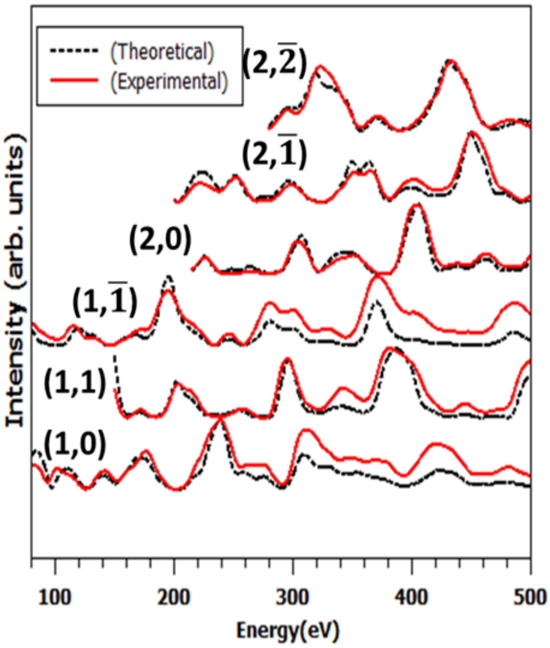

Fig. 2. Theoretical and experimental I(E) curves. (Pendry R-Factor, Rp = 0.12)

Earlier theoretical works [3,4] did not include a wide range of data as shown in this investigation report. The procedure involves calculation of the intensity values for different energies by the provided parameters, followed by iterations.

5.2 Structural Model of the Mo(110)

The atomic structure from the top view can be observed in Fig. 3.

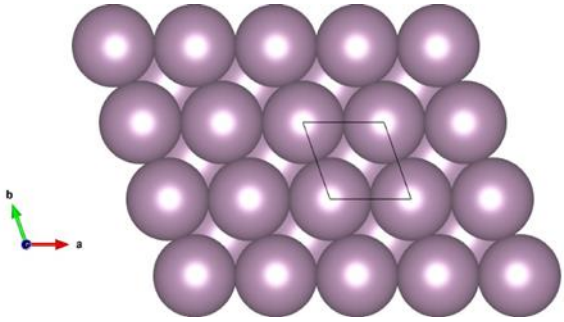

Fig. 3. Top view of the p(1×1) structure of Mo(110).

The interlayer spacings have been calculated from the atomic positions which is shown in Fig. 4.

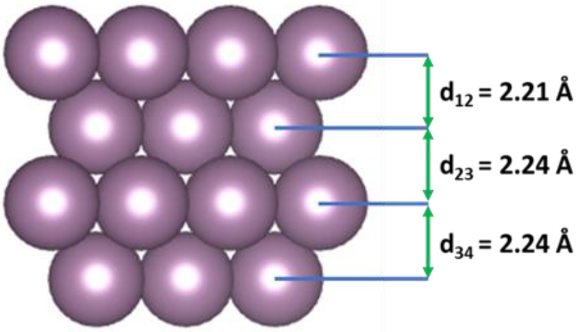

Fig. 4. Side view of the p(1×1) structure of Mo(110) showing the approximate interlayer spacings.

Due to the presence of the dangling bonds on the surface layer atoms, internal stress always exists. The amount of atomic inter-layer relaxation can be calculated by comparing with the ideal bulk Mo material i.e. $(\Delta d/d)$ for each layer where Δd corresponds to change in interlayer distance with respect to ideal bulk condition. Investigation of this atomic inter-layer relaxation combined with the unit cell parameters is important in order to study adsorption on the surface at atomic level.

The first interlayer (d_{12}) relaxation by contraction is found to be 0.9%. In order to compensate for the interlayer contraction between the first layer and the second layer, expansion relaxation must exist in the following layers i.e. d_{23} and d_{34}. The interlayer relaxation between 2nd and 3rd layers i.e. d_{23} and d_{34} is found to be 0.45% each. It can be observed that stress is released due to interlayer relaxation with compensation between the layers at the surface. This observation also validates the atomic model which is obtained by fitting the theoretical model with experimental observation with good agreement. The inter-layer relaxation of the Mo(110) layer is found to be very less.

5.3 Deposition of Sn on the Mo(110)

Attempts to achieve Sn layer over Mo(110) have been successful which can be observed by LEED patterns as shown in Fig. 5. The LEED patterns of Sn-superstructures on the Mo(110) surface depend on the coverage, Sn-flux, deposition time and temperature based on the LEED patterns achieved by Tikhov and Bauer [9] without evidence for their proposed models as mentioned earlier. Sn has been evaporated from Sn-source and directly incident on clean Mo(110). As a result of which, we could observe the LEED patterns for the Sn-superstructures. Lower coverage with elevated temperatures results in the Mo(110)-(3×2)-Sn structure which is found to be a stable structure. On the other hand, at room temperature, higher coverage of Sn-flux on Mo(110) leads to the formation of Mo(110)-(1×3)-Sn and Mo(110)-(1×4)-Sn structures. The Mo(110)-(1×4)-Sn structure requires much higher coverage which is evident from the amount of flux used in comparison to Mo(110)-(1×3)-Sn. “High temperature” or “elevated temperature” which is referred as temperatures higher than room temperature while adsorption of Sn on Mo(110) may not be confused with “annealing” of structures after the adsorption of Sn-superstructure over the Mo(110) surface. While the Mo(110)-(3×2)-Sn structure has been deposited at elevated temperature >125°C as a necessary deposition condition, the Mo(110)-(3×3)-Sn structure has been achieved by “annealing” the Mo(110)-(1×4)-Sn structure after the formation of the Mo(110)-(1×4)-Sn structure. It implies that, the Mo(110)-(3×3)-Sn structure is formed by restructuring or rearrangement of atoms of the Mo(110)-(1×4)-Sn structure without addition of Sn-atoms into the superstructure. Thus the Mo(110)-(3×3)-Sn structure is also supposed to consist of larger and more stable domain structure as compared to Mo(110)-(1×4)-Sn structure. As the Mo(110)-(3×2)-Sn structure requires higher temperature during the adsorption process, alloy formation is expected by replacing of the atoms from the Mo(110) surface. The Mo(110)-(1×3)-Sn structure contains smaller domains as compared to Mo(110)-(1×4)-Sn structure as the former was formed at very low Sn-flux (<5 nA) as compared to the later one. Thus the adsorption of Sn over Mo(110) was as per expected. The depositions were attempted multiple times to optimize the parameters for adsorption of the various structures.

Our next aim is to prepare structural models for the different Sn-superstructures to understand the domains related to each structure. We’ll use the same tensor LEED package which is used to determine the position of the atoms of clean Mo(110). We’ll try to determine the model by optimizing the lattice sites of the atoms in the crystal structures. The proposed crystal structures of Sn on Mo(110) surface will consist of the relaxed atomic layers of the Mo(110) surface along with the adsorbed Sn-atoms. To achieve the model crystal structure, similar analysis procedure will be carried out. Consequently, the I(E) curves for the proposed model structures of Sn-superstructure over Mo(110) will have to agree with the experimentally observed curves.

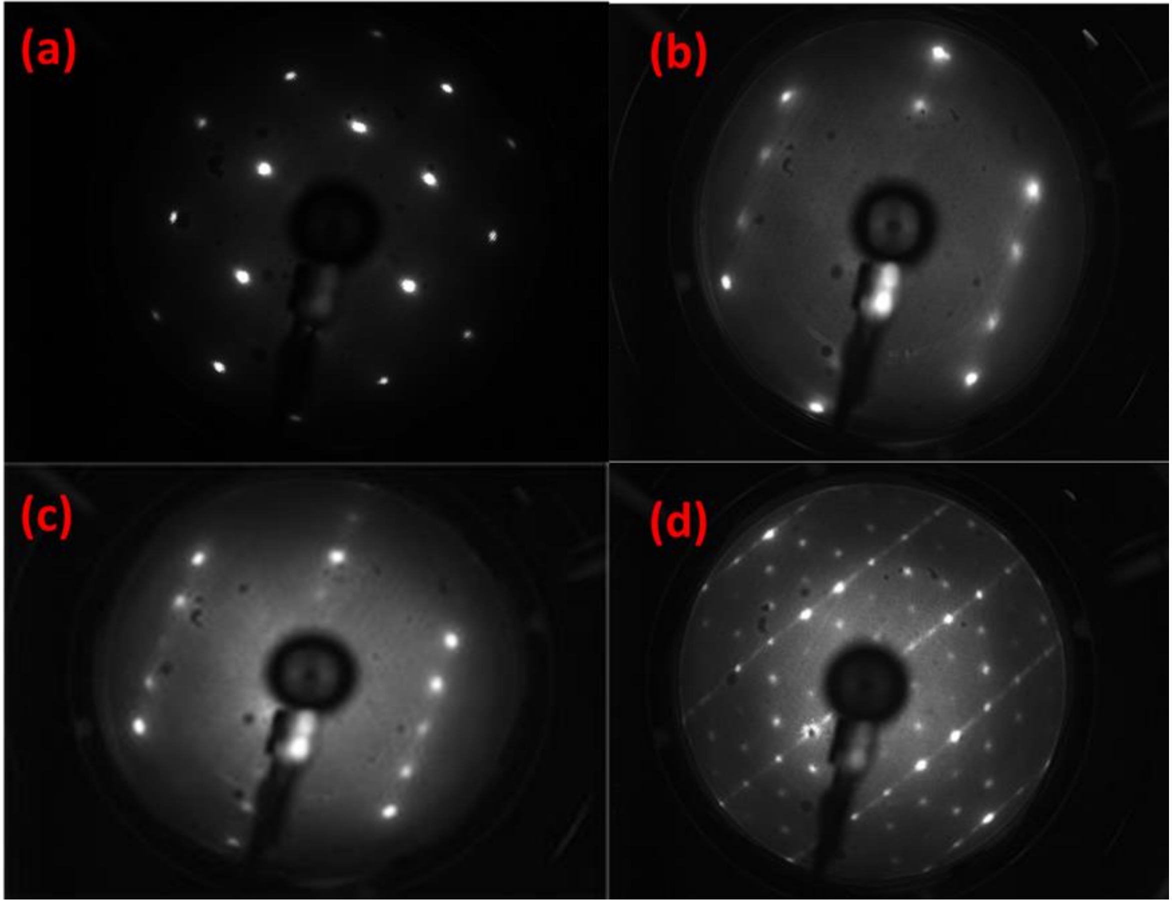

Fig. 5: LEED spectra for Sn superstructures on Mo(110). Various LEED patterns can be observed viz: (a) 3×2 (80 eV) (b) 1×3 (78 eV) (c) 1×4 (77 eV) (d) 3×3 (135 eV) which depends on coverage, temperature, exposure time.

5.4 Calculation of Density of States (DoS): Computational methodology

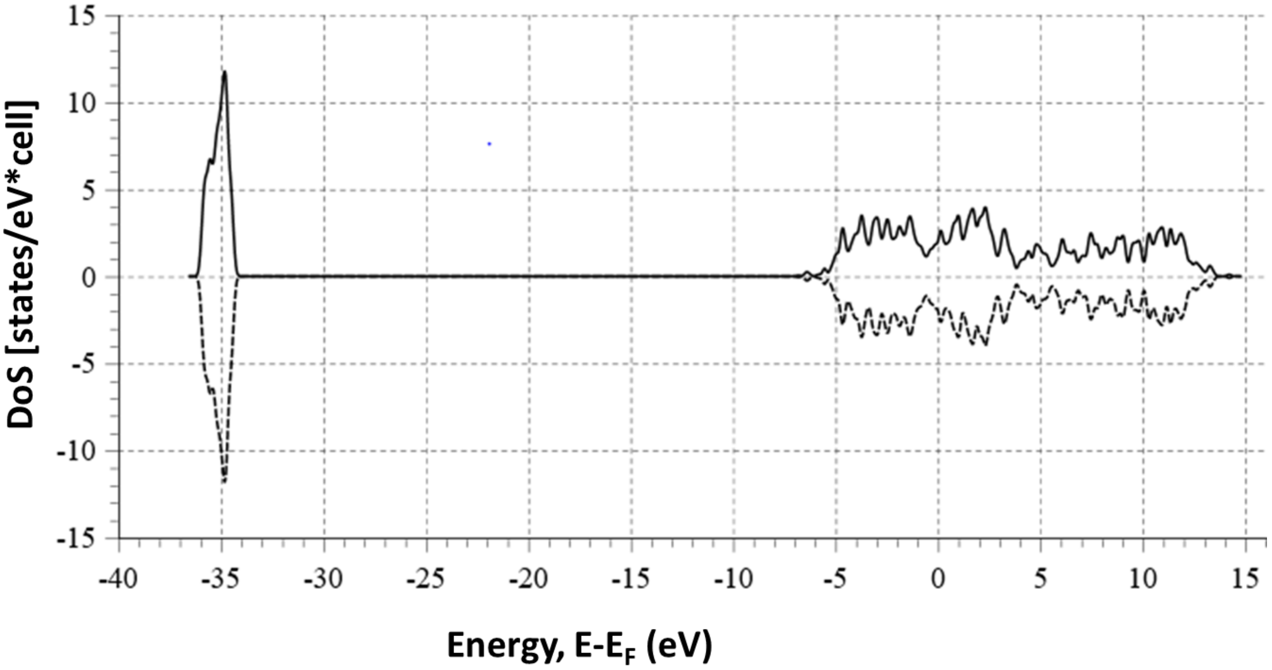

Fig. 6: Calculation of the electronic density of states (DoS) of the clean Mo(110). The continuous lines of the energy states (DoS) >0 represents the up-spin while the dashed lines with energy states (DoS) <0 represents the down-spin.

In this work we've tried to observe the electronic density of states for the combined effect of the first four layers where the surface relaxation exists and represented by the unit cell of the surface crystal structure i.e., Mo(110). The distribution of the Electronic density of states (DoS) can be expressed as $D(E) = N(E)/V$, where $N(E)\delta E$ represents the total number of states within the system of volume (V) with energy ranging from E to $E+\delta E$. The total distribution of the DoS of the unit cell for Mo(110) surface is calculated which shows the distribution of available energy states for occupation within the specified range of energy.

From the DoS distribution in Fig. 6, we can observe that, in the vicinity of Fermi energy (E_F) within range of -15 eV and 15 eV, the electronic energy states or bands only exist up to 4 eV, which is the highest occupied energy level within the given range of simulations. The DoS is continuous as the crystal structure is not an isolated system.

The DoS will be modified when an adsorbate atom will be added to the crystal structure as heterogeneous system. The variation of the DoS with addition of an adsorbate atom will give the effect of the adsorbate atom on the overall electronic structure of the lattice (surface + adsorbate).

6. CONCLUSIONS

We have investigated the multilayer surface relaxation of Mo(110) by LEED I(E) analysis. The Pendry R-factor (R_p) is found to be 0.12 which is a good agreement between calculated data and experimental observation. The multilayered atomic model of the Mo(110) surface is shown here. We've calculated the atomic intra-layer relaxations. Our investigation reveals that the contraction due to the first interlayer i.e., d_{12} which is 0.9% is compensated by the 2nd and 3rd interlayer i.e., 0.45% each.

Our LEED analysis involves larger energy range in comparison to earlier investigations [3,4] which results in higher accuracy of the proposed model and relaxations of atomic layers. We've successfully optimized the adsorption parameters of Sn over Mo(110). We have been successful to achieve different Mo-superstructures of Sn over Mo(110) viz. Mo(110)-(3×2)-Sn, Mo(110)-(1×3)-Sn, Mo(110)-(1×4)-Sn, Mo(110)-(3×3)-Sn at different coverages/temperatures. The different superstructures of Sn over Mo(110) are dependent on various parameters such as deposition time, Sn-flux, temperature. We've also calculated the density of states (DoS) for the unit cell of the multilayered crytal structure which gives an insight into the available energy states for electrons by ab-initio first principle DFT calculations.

The atomic model for the Mo(110) surface has been accomplished by using the symmetrized and automated tensor LEED package formulated by Barbieri/Van Hove as mentioned and the DFT calculations were accomplished by BURAI 1.3 suite which is a GUI of Quantum ESPRESSO.

Our future endeavour includes determination of the lattice sites for the adsorbate Sn-atoms on the Mo(110) structure follwed by density functional theory calculations.

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