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Banik, Dhiman
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Nagamatsu, Yuka
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Jimba, Tomoya
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

Nakagawa, Takeshi
Interdisciplinary Graduate School of Engineering Sciences, Kyushu University

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Dhiman Banik*, Yuka Nagamatsu, Tomoya Jimba and Takeshi Nakagawa
Interdisciplinary Graduate School of Engineering Sciences, 6-1 Kasuga-koen, Kasuga, Fukuoka 816-8580, Kyushu University, Japan.
*Corresponding author email: dhiman.academic@gmail.com, dhiman@kyudai.jp

Abstract: *Herein we report the atomic model of pseudomorphic Fe monolayer on Ru(0001) surface analyzed by low energy electron diffraction (LEED) followed by the formation of c(4×2) structure upon exposure to oxygen. After deposition of the Fe overlayer on Ru(0001) surface at room temperature, the prepared surface was exposed to molecular oxygen (O_2). When 2 Langmuir of O_2 is introduced at room temperature on the prepared Fe(111)/Ru(0001) surface, the pseudomorphic p(1×1) structure of the Fe monolayer on the Ru(0001) surface changes to c(4×2) structure.*

Keywords: pseudomorphic Fe monolayer, Ru(0001) surface, LEED, oxygen adsorption, c(4×2) structure

1. INTRODUCTION

Thin films and monolayers of transition metals such as Fe, Sn, and their oxides are always of great interest due to their physical and chemical properties. Remarkable progress has been made in the field of epitaxial growth of films over single crystal substrates with precise control of the atomic layers. Ultra-thin transition metals on metal substrates are always of great interest along with the growth of magnetic nanostructures. Modern ultra-high vacuum (UHV) systems, in conjunction with surface cleaning procedures, have enabled the deposition of monolayer atoms on a clean surface using very simple procedures. Although Fe is a prototypical ferromagnet, it becomes an antiferromagnet when stabilized in the metastable FCC phase [1-3]. Monolayer Fe on Ru(0001) is not expected to exhibit ferromagnetism due to hybridization between Fe and Ru resulting in a magnetic 'dead layer' and evidence of alloy formation upon annealing of the Fe layers also have been found [4,5].

C. Liu and S. D. Bader also confirmed epitaxial growth of Fe on Ru(0001) at room temperature but found the first two layers to be epitaxially grown followed by a gradual development of disorders despite the absence of new diffraction spots [5]. Egawa et al. also investigated epitaxial Fe on Ru(0001), finding a two-dimensional layer-by-layer (Frank-Van der Merwe) mechanism on a Ru(0001) surface and only the first monolayer (1 ML) of Fe was found to be commensurate FCC p(1×1) Fe(111) similar to the hexagonal structure of the substrate, which relaxes to incommensurate BCC Fe(110) structure at coverages above 1 ML. Annealing at high temperatures has also been found to affect the overlayer Fe structure, as the Fe atoms tend to diffuse into the Ru substrate, possibly due to their smaller size [6]. D.Tian et al. conducted qualitative and quantitative analyses of Fe on Ru(0001) growth studies and observed the Stranski-Krastanov mode of growth, which is monolayer growth followed by island growth. But the island growth was incommensurate BCC Fe(110) which are three-dimensional domains in all possible orientations being compatible with the 3-fold hexagonal symmetry of the Ru(0001) substrate [7]. These occurrences can be attributed to the strain originating from the lattice mismatch between the adsorbent and the adsorbate.

Several studies show that the magnetization of Fe varies with substrate type and layer count, with deposition temperatures also influencing the structural quality of the films [8-15]. V.Martin et al. studied the pseudomorphic growth of Fe monolayers on reconstructed Ir(001)-(1×1) surfaces at 90 K to avoid increased roughness at room temperature [16].

Oxides of Fe are also an important material and find applications. The formation of different types of oxides such as FeO, Fe_3O_4, etc. is feasible depending on the growth conditions. Guido Ketteler and Wolfgang Ranke found that annealing of FeO(111) films on Ru(0001) with thickness of more than one monolayer leads to the nucleation of small Fe_3O_4(111) islands which continues to grow in size and number upon prolonged oxidation [17]. I Palacio et al. investigated the initial stages of FeO growth on the Ru(0001) surface by simultaneous deposition of iron and oxygen at elevated temperatures where FeO grows by nucleation followed by spreading of bilayer thick islands which eventually coalesce under influence of oxygen pressure. With oxygen pressure of 10^{-6} Torr, the islands were found to be bilayer thick (Fe–O–Fe–O) but on the contrary, under a pressure of 10^{-8} Torr, the islands were found to be single FeO layer thick [18]. FeO is known as a Mott insulator and the elucidation of insulating phases of such crystals with partially filled d-orbitals has been attempted by N.F Mott and Z.Zinamon [19].

Oxygen atoms can also stick to the surface by dissociative chemisorption, a surface phenomenon. The dissociative chemisorption of O_2 can be interpreted in terms of a 'mobile molecular precursor' as an extrinsic molecular precursor [20]. A.Hodgson et al. experimentally studied the dissociative chemisorption of O_2 on Fe(110) where the initial sticking probability of O_2 is found to be slightly increased with a decrease in temperature and increased probability of dissociation with higher O-coverage [21]. G. Worthy et al. found the initial sticking probability to be 0.42 which gradually falls with the increasing coverage to minimum value before rising slightly followed by a final slow decrease with the saturation of the surface at higher exposures, and the sticking coefficient also increases with decrease in surface temperature [22]. V.S. Smentkowski et al. earlier studied the interaction of O_2 with Fe(110) at a wide temperature range of 90 to 920 K where the formation of Fe_3O_4 has been found as the final oxide layer at saturation of O_2 above 90 K and temperatures higher than ~ 700K, Fe_3O_4 tends to convert into FeO due to diffusion of Fe into the Fe_3O_4 overlayer from the Fe(110) crystal [23].

Koutaro Nishihara et al. investigated the oxygen-induced surface structures on the Fe(110) layer and found two chemisorbed LEED structures, p(2×2) and p(3×2). Due to steric repulsion, oxygen was found to move from long bridge sites in the case of the p(2×2) structure to three-fold hollow sites in the case of the p(3×2) structure as oxygen coverage increases [24]. Aside from oxygen adsorption on Fe(110), co-adsorption of K with O has also been attempted on the Fe(110) surface, where an ordered c(4×2) LEED structure with oxygen coverage of 0.5 and potassium coverage of 0.28 was formed [25].

The oxygen-adsorbed structure can also enhance the catalytic activity of the Fe surface. When oxygen has been introduced on an annealed Fe(111) surface, c(4×2) LEED pattern was generated due to dissociative chemisorption on the surface which enhanced the dissociation of ammonia by 3.5 times by co-adsorption of oxygen [26]. Senzi Li et al. studied the site requirements in the iron-catalyzed Fischer-Tropsch synthesis process and observed that removing a small fraction of the lattice oxygen atoms in the Fe_2O_3 structure, corresponding to ∼1 equivalent monolayer, is required for the process of active site formation [27].

Strain is also considered an important factor for surface adsorption and the formation of oxides. Despite a large lattice mismatch of 10%, FeO can grow on W(110) [28]. The inertness of Fe(110) towards N_2 adsorption disappears on Fe/W(110) as N_2 dissociation will occur when the individual N-surface atoms' attraction overcomes the strong N-N interaction [29, 30] which implies that local strain changes the reactivity of surfaces. The formation of surface overlayers can be identified by the dynamic LEED analysis technique which also includes the diffraction pattern from the crystal surface [31] involved as it is a very powerful technique to investigate the atomic geometry of crystalline surfaces. Herein we will discuss the details of the pseudomorphic Fe monolayer of the Fe(111)/Ru(0001) structure and adsorption of oxygen on its surface which is required to understand the interaction of oxygen with the Fe(111) monolayer. Also, the pseudomorphic Fe(111) monolayer has been investigated to determine the surface atomic structure of the chemisorbed oxygen atoms.

2. EXPERIMENTAL PROCEDURE

The surface was cleaned by repeated cycles of oxidation (at 1200 °C under O_2 pressure of ~5×10^{-6} Pa) followed by flash desorption (1500 °C at <6×10^{-8} Pa) to remove the surface impurities and the chemically bonded oxygen on the surface**.** Deposition of an epitaxial monolayer of Fe(111) on Ru(0001) surface has been accomplished under UHV conditions (<6×10^{-8} Pa) with a deposition rate of 0.1ML/minute which is followed by exposure to ~2 Langmuir of Oxygen to get the oxygen adsorption structure at room temperature. The Fe-flux has been checked by quartz crystal microbalance (QCM). The LEED pattern was recorded with the help of a digital charge-coupled device (DCCD) camera integrated with a digitally software-aided data acquisition system. The variation of intensity with the energy of the incident electron beam i.e. *I(E)* curves was generated for the pseudomorphic Fe(111) monolayer on Ru(0001).

3. STRUCTURAL CALCULATION

To analyze the structure of the formed overlayer, we've used the symmetrized and automated tensor LEED package formulated by Barbieri/Van Hove [32]. The imaginary part of the inner potential (V_ω) was fixed at -5.0 eV and we've determined the real part by fitting the theoretical calculation with the experimentally observed data. The agreeing structural model exhibits a unique and lowest Pendry reliable factor (R_p) which will be the best fit among all the structural models by a fair margin [33]. The error bar in structural parameters was calculated by the variance of R_p,

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

where R_{min} is the lowest Rp value and ΔE is the total the energy range of the experimental *I(E)* curves [33].

4. RESULTS & DISCUSSION: Analysis of the LEED pattern and determination of the structural model.

After achieving a clean Ru(0001) surface, the LEED pattern is generated for the same, as shown in Fig.1,2. The unit cell of the p(1×1) pseudomorphic structure is also shown by the red diamond in Fig.2(b) for the LEED pattern at 220 eV. The atomic structural model of the Fe(111) monolayer, as well as the 6 layers of Ru(0001), is shown in Fig.3. The top view of the Fe monolayer surface is shown in Fig.3(a) which also shows the unit cell in real space and the side view of the atomic structural model is shown in Fig.3(b) which shows the atomic interlayer spacing. The interlayer spacing between Ru layers, i.e. the Ru-Ru interlayer distance, is found to be ~2.14 Å. It is comparatively larger than that of the Fe and Ru interlayer distance, which is found to be 2.05 Å after the trial-and-error method which is the same as the previous report [7]. The LEED *I(E)* analysis of the Fe(111)/Ru(0001) structure is shown in Fig.4, which gives a Pendry R-Factor (R_p) of 0.19. It indicates a better agreement between experimental and theoretical data when compared to the previous report where the R_p was 0.29 [7]. The formation of the c(4×2) structure, which is achieved without annealing at room temperature is illustrated in Fig.5. After the formation of Fe(111) monolayer on the Ru(0001) surface, no additional LEED spots were observed but there was a change in background intensity as shown in Fig.5(b) in comparison to that of the clean surface in Fig.5(a). The *I(E)* curves of the Fe(111)/Ru(0001) structure as shown in Fig.4 are different from that of the clean Ru(0001) surface [34] due to the formation of the Fe overlayer. After that, the Fe(111) overlayer was exposed to oxygen for the dissociative chemisorption process. The LEED pattern of the c(4×2) structure is shown in Fig.5 (c) at 74eV and Fig.6 at 90 eV and 220 eV, which agrees with the previous report [26]. The c(4×2) LEED pattern, as shown in Fig.6, provides evidence of chemisorbed oxygen on the epitaxial Fe(111) monolayer at room temperature due to the appearance of additional LEED spots. As the structural transformation from chemisorbed to oxidation state requires investigation, including the effect of strain, the atomic structural model of the c(4×2) LEED pattern must be determined by *I(E)* analysis.

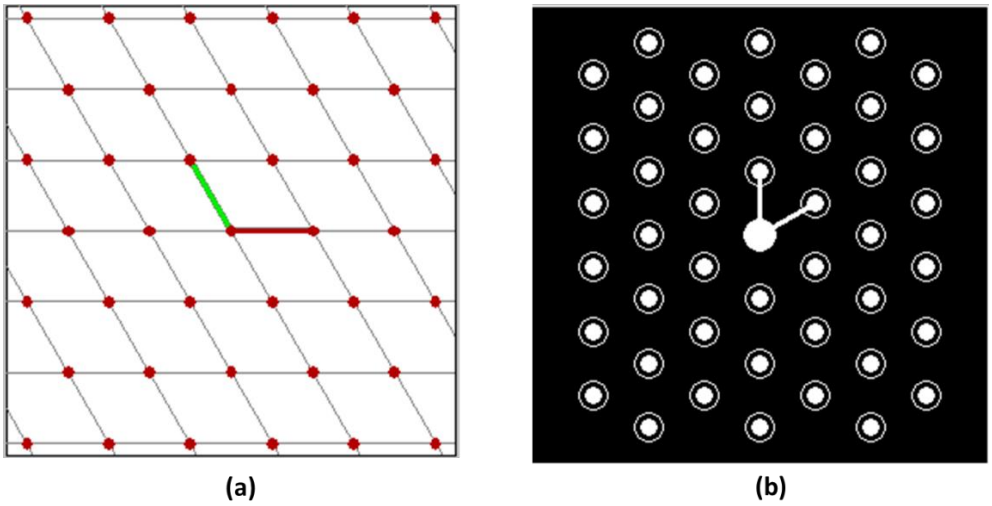

Fig. 1. Simulated (a) surface lattice (real space) and (b) LEED pattern (reciprocal space) for the Ru(0001) surface and Fe(111)/Ru(0001) pseudomorphic structure.

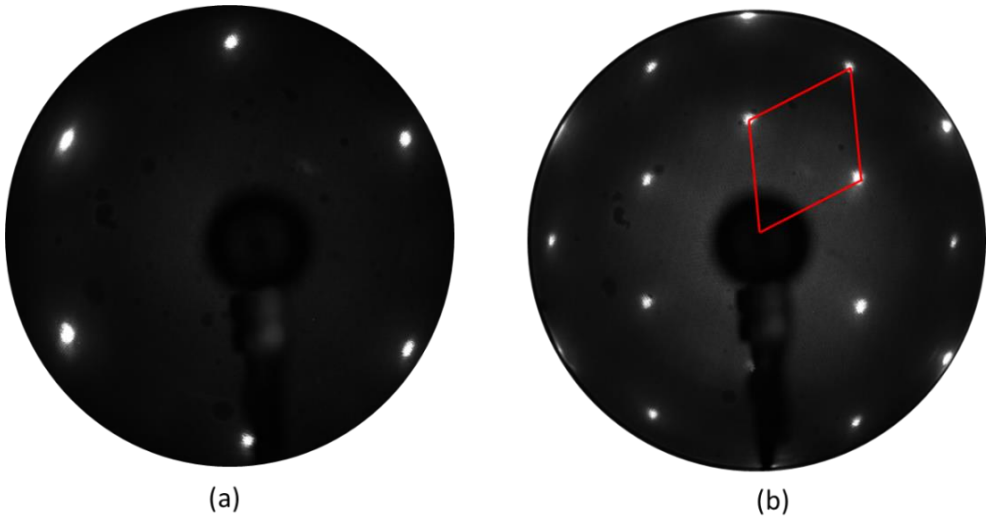

Fig. 2. LEED pattern of clean Ru(0001) surface at (a) 90 eV, (b) 220 eV over which Fe was deposited. The unit cell in the reciprocal space is shown by the red diamond. The LEED pattern is unaltered with pseudomorphic monolayer growth of Fe.

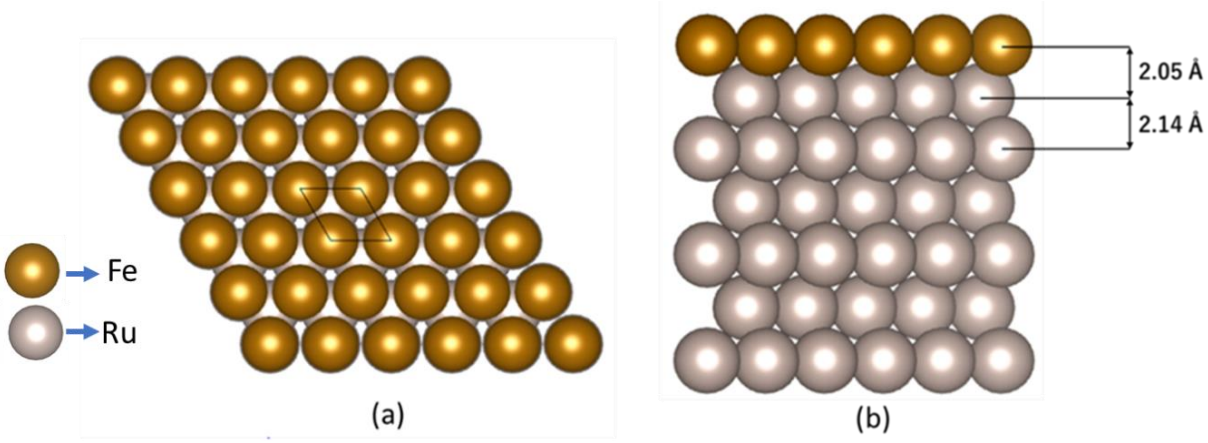

Fig. 3. Atomic model of the pseudomorphic Fe(111) monolayer on Ru(0001) surface i.e. the Fe(111)/Ru(0001) structure: (a) Top view where the unit cell is represented by the black diamond (b) Side view where the interlayer distances are shown. The formed Fe monolayer is commensurate with the Ru(0001) surface.

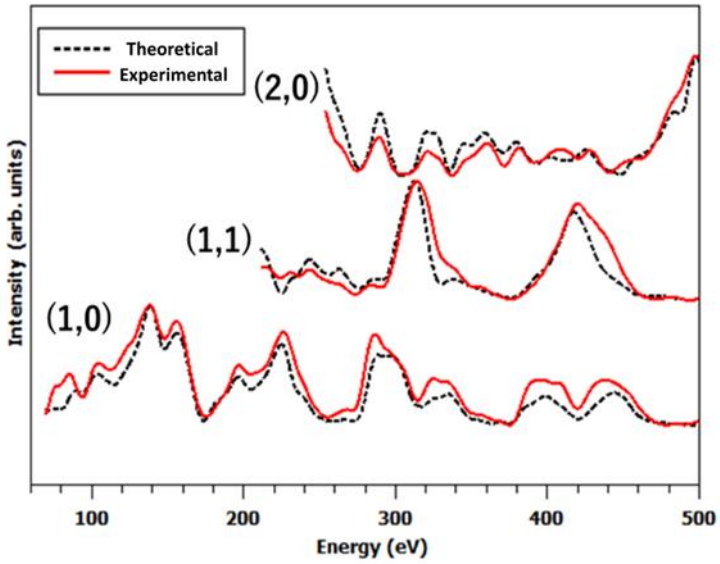

Fig. 4. LEED *I(E)* analysis of the atomic model shown in Fig. 3. reveals an acceptable Pendry R-Factor (R_p) of 0.19 for the Fe(111)/Ru(0001) structure.

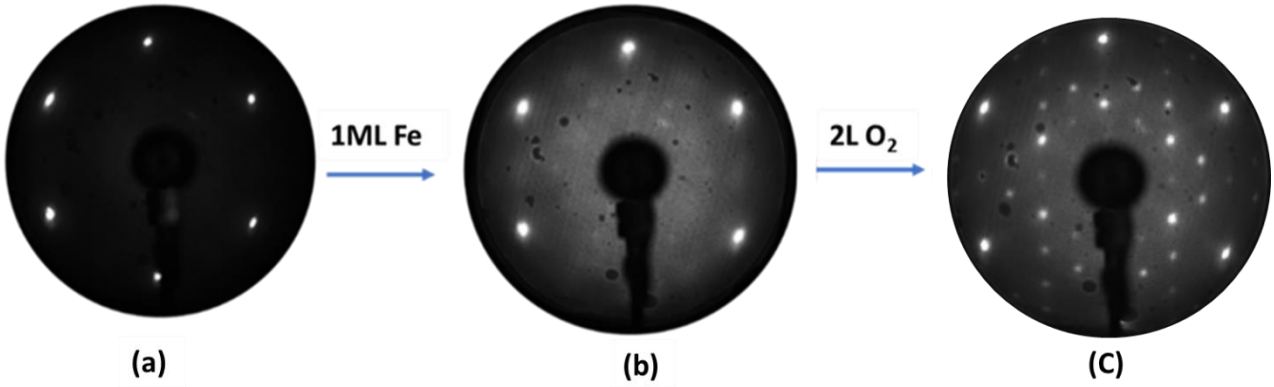

Fig. 5. LEED pattern of the c(4×2) structure is observed as expected [26] after exposure to 2 Langmuir of oxygen on pseudomorphic monolayer of Fe on Ru(0001). The LEED pattern at 74 eV of (a) Clean Ru(0001) structure (b) pseudomorphic Fe(111)/Ru(0001) structure where a brighter background is observed as compared to the LEED pattern of clean Ru(0001) structure (c) c(4×2) structure where additional diffraction spots can be observed as expected.

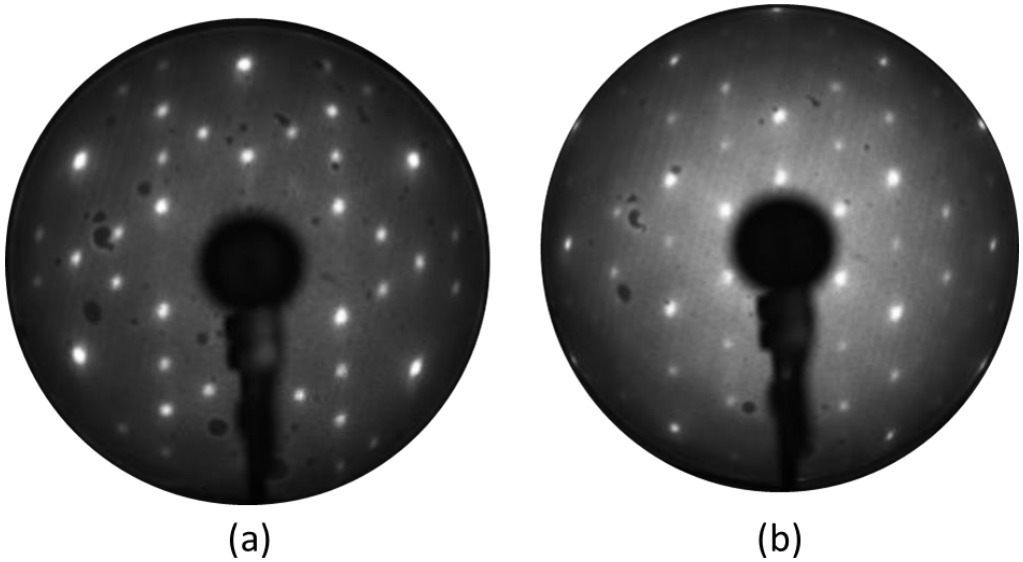

Fig. 6. LEED pattern of the c(4×2) structure at (a) 90 eV, (b) 220 eV

5. CONCLUSION

We have deposited a pseudomorphic monolayer of Fe(111) on Ru(0001) surface with an acceptable Pendry R-Factor (Rp) of 0.19 for LEED *I(E)* analysis, demonstrating comparatively better agreement in terms of Pendry R-Factor (Rp) between theoretical and experimental data in comparison to the previous report. We've also successfully optimized the oxygen adsorption conditions for dissociative chemisorption, as made evident by the clear LEED pattern of the c(4×2) structure observed after exposing the formed pseudomorphic monolayer Fe(111) under UHV conditions to ~2 Langmuir of oxygen at room temperature. These findings will prompt further research into the structural stability of FeO on other surfaces. Our next endeavor will be a detailed analysis of the formed surface structure of the adsorbed oxygen on the pseudomorphic Fe(111) layer and attempts to prepare FeO on surfaces other than Ru(0001). The stability of the chemisorbed surface structure needs to be investigated as well, which will also lead to more research into the structural stability of strained FeO on other transition metal surfaces.

6. REFERENCES:

[1] S. C. Abrahams, L. Guttman, J. S. Kasper, “Neutron diffraction determination of antiferromagnetism in face-centered cubic (γ) iron,” Phys. Rev., vol. 127, no. 6, pp. 2052–2055, 1962.

[2] U. Gonser, C. J. Meechan, A. H. Muir, and H. Wiedersich, “Determination of néel temperatures in fcc iron,” J. Appl. Phys., vol. 34, no. 8, pp. 2373–2378, 1963.

[3] R. Halbauer and U. Gonser, “Antiferromagnetism of fcc iron films,” J. Magn. Magn. Mater., vol. 35, pp. 55–56, 1983.

[4] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, “Local magnetic moment associated with an iron atom dissolved in various transition metal alloys,” Phys. Rev., vol. 125, no. 2, pp. 541–552, 1962.

[5] C. Liu and S. D. Bader, “Magnetic properties of ultrathin fcc Fe(111)/Ru(0001) films,” Phys. Rev. B, vol. 41, no. 1, pp. 553–556, 1990.

[6] C. Egawa, T. Aruga, and Y. Iwasawa, “Epitaxial growth of Fe overlayers on the Ru(001) surface,” Surf. Sci., vol. 188, no. 3, pp. 563–574, 1987.

[7] D. Tian, H. Li, F. Jona, and P. M. Marcus, “Study of the growth of Fe on Ru(0001) by low-energy electron diffraction,” Solid State Commun., vol. 80, no. 10, pp. 783–787, 1991.

[8] R. Wu and A. J. Freeman, “Magnetic properties of Fe overlayers on W(001) and the effects of oxygen adsorption,” Phys. Rev. B, vol. 45, no. 13, pp. 7532–7535, 1992.

[9] A. Kubetzka et al., “Revealing antiferromagnetic order of the Fe monolayer on W(001): Spin-polarized scanning tunneling microscopy and first-principles calculations,” Phys. Rev. Lett., vol. 94, no. 8, pp. 2–5, 2005.

[10] N. Petersen, S. Meyer, and S. Heinze, “Tuning exchange interactions in antiferromagnetic by transition-metal overlayers,” Phys. Rev. B, vol. 104, no. 10, pp. 1–11, 2021.

[11] C. Liu and S. D. Bader, “Perpendicular surface magnetic anisotropy in ultrathin epitaxial Fe films,” J. Vac. Sci. Technol. A Vacuum, Surfaces, Film., vol. 8, no. 3, pp. 2727–2731, 1990.

[12] C. A. Ballentine, R. L. Fink, J. Araya-Pochet, and J. L. Erskine, “Exploring magnetic properties of ultrathin epitaxial magnetic structures using magneto-optical techniques,” Appl. Phys. A Solids Surfaces, vol. 49, no. 5, pp. 459–466, 1989.

[13] B. Hardrat, A. Al-Zubi, P. Ferriani, S. Blügel, G. Bihlmayer, and S. Heinze, “Complex magnetism of iron monolayers on hexagonal transition metal surfaces from first principles,” Phys. Rev. B - Condens. Matter Mater. Phys., vol. 79, no. 9, pp. 1–5, 2009.

[14] C. Li, A. J. Freeman, H. J. F. Jansen, and C. L. Fu, “Magnetic anisotropy in low-dimensional ferromagnetic systems: Fe monolayers on Ag(001), Au(001), and Pd(001) substrates,” Phys. Rev. B, vol. 42, no. 9, pp. 5433–5442, 1990.

[15] Y. Xu, E. Kernohan, D. Freeland, A. Ercole, M. Tselepi, and J. Bland, “Evolution of the ferromagnetic phase of ultrathin Fe films grown on GaAs(100),” Phys. Rev. B - Condens. Matter Mater. Phys., vol. 58, no. 2, pp. 890–896, 1998.

[16] V. Martin et al., “Pseudomorphic growth of Fe monolayers on Ir (001) - (1×1): From a fct precursor to a bct film,” Phys. Rev. B - Condens. Matter Mater. Phys., vol. 76, no. 20, pp. 1–9, 2007.

[17] G. Ketteler and W. Ranke, “Heteroepitaxial growth and nucleation of iron oxide films on Ru(0001),” J. Phys. Chem. B, vol. 107, no. 18, pp. 4320–4333, 2003.

[18] I. Palacio, M. Monti, J. F. Marco, K. F. McCarty, and J. De La Figuera, “Initial stages of FeO growth on Ru(0001),” J. Phys. Condens. Matter, vol. 25, no. 48, 2013.

[19] N. F. Mott and Z.Zinamon, "The metal-nonmetal transition", Rep. Prog. Phys., vol. 33, no. 3, pp. 881-940, 1970.

[20] M. Arbab and J. B. Hudson, “The kinetics and mechanism of oxygen uptake on a polycrystalline iron surface,” Surf. Sci., vol. 206, no. 1–2, pp. 317–337, 1988.

[21] A. Hodgson, A. Wight, and G. Worthy, “The kinetics of O2 dissociative chemisorption on Fe(110),” Surf. Sci., vol. 319, no. 1–2, pp. 119–130, 1994.

[22] G. Worthy, C. Cottrell, A. Wight and A. Hodgson Dissociation of O_2 on Fe(110), Surf. Rev. Lett., Vol. 01, No. 04, pp. 501-503, 1994.

[23] V. S. Smentkowski and J. T. Yates, “The adsorption of oxygen on Fe(110) in the temperature range of 90 to 920 K,” Surf. Sci., vol. 232, no. 1–2, pp. 113–128, 1990.

[24] K. Nishihara, T. Nomitsu, T. Nakagawa, and S. Mizuno, “Structural investigation and magnetic properties of oxygen adsorption on ultrathin Fe(110) film,” Surf. Sci., vol. 685, no. December 2018, pp. 34–39, 2019.

[25] G. Pirug, G. Brodén, and H. P. Bonzel, “Coadsorption of potassium and oxygen on Fe(110),” Surf. Sci., vol. 94, no. 2–3, pp. 323–338, 1980.

[26] C. Egawa, K. Sawabe, and Y. Iwasawa, “Adsorption and decomposition of ammonia on an Fe(1 × 1)

overlayer on an Ru(001) surface with or without co-adsorbed oxygen," J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases, vol. 84, no. 1, pp. 321–330, 1988.
[27] S. Li, W. Ding, G. D. Meitzner, and E. Iglesia, "Spectroscopic and transient kinetic studies of site requirements in iron-catalyzed Fischer-Tropsch synthesis," J. Phys. Chem. B, vol. 106, no. 1, pp. 85–91, 2002.
[28] K. Freindl et al., "Oxygen on an Fe monolayer on W(110): From chemisorption to oxidation," Surf. Sci., vol. 617, pp. 183–191, 2013.
[29] K. Homann, H. Kuhlenbeck, and H. J. Freund, "N2 adsorption and dissociation on thin iron films on W(110)," Surf. Sci., vol. 327, no. 3, pp. 216–224, 1995.
[30] I. Goikoetxea, J. I. Juaristi, R. Díez Muiño, and M. Alducin, "Surface strain improves molecular adsorption but hampers dissociation for N2 on the Fe / W (110) surface," Phys. Rev. Lett., vol. 113, no. 6, pp. 1–5, 2014.
[31] D. Banik, S. Hossain, C. Xiaobin, and T. Nakagawa, "Surface Relaxation of Clean Mo (110), Optimization of Sn Adsorption and Ab-Initio Calculation of The Electronic Density of States (DoS)," in Proceedings of International Exchange and Innovation Conference on Engineering & Sciences (IEICES), 2021, vol. 7, pp. 39–44.
[32] M. A. Van Hove et al., "Automated determination of complex surface structures by LEED," Surf. Sci. Rep., vol. 19, no. 3–6, pp. 191–229, 1993.
[33] J. B. Pendry, "Reliability factors for LEED calculations," J. Phys. C Solid State Phys., vol. 13, no. 5, pp. 937–944, 1980.
[34] P. J. Feibelman, J. E. Houston, H. L. Davis, and D. G. O'Neill, "Relaxation of the clean, Cu- and H-covered Ru(0001) surface," Surf. Sci., vol. 302, no. 1–2, pp. 81–92, 1994.