

# Atomic-level characterization of metal/oxide interfaces (Ti, Fe, Ni, Ag, Au/Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>): a background for nanomaterial design for catalysis to photonics

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## ABSTRACT

Surface sensitive techniques – Auger electron, X-ray photoelectron and high resolution electron energy loss spectroscopies (AES, XPS, HREELS), low energy ion scattering (LEIS), reflection absorption infrared spectroscopy (RAIRS), low energy electron diffraction (LEED) – were used to study adsorption of submonolayer films of Ti, Fe, Ni, Ag, Au on the surface of aluminium, magnesium and titanium oxide films in-situ grown on the Mo(110) support. Separated metal atoms and small clusters, deposited on oxide supports, acquire cationic character, presumably due to interaction with surface defects. As the defects are being covered with increasing of the surface concentration of metal atoms, their effect decreases, so the interface charge transfer effect weakens, further accompanied by lateral depolarization of adatoms at higher coverage. Choosing atomic structure, morphology, relative content and nature of supported metal/oxide structures allows precise tuning of their electronic, catalytic and optical properties crucial, for new technological applications.

**Keywords:** adsorption, surface reaction, oxide supported metal films, metal/oxide interface, surface science techniques.

## 1 INTRODUCTION

Metal/oxide systems are widely used in different application fields, such as heterogeneous catalysis, nanoelectronics, sensing techniques, optics, photonics, etc. [1,2]. Particularly interesting are those consisting of nanosized metal particles, deposited on oxide supports. This topology offers at least two-fold advantage, arising from a specific size effect of metal cluster, on one hand, and the contact perimeter interface effect – on the other. Despite of a very extensive research in this field, the main challenge is still detail atomic level understanding of the physical and chemical effects in such systems – the effects which determine the technological relevance of metal/oxide

structures. In relation to this, the aim of the present work was to determine the properties of metal nanoclusters (Ti, Fe, Ni, Ag, Au) deposited on oxide supports (Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>), and of the corresponding metal/oxide interface. The choice of these materials is motivated by the fact that transition and noble metals offer a wealth of phenomena due to their specific electronic structure, on one hand, and a variety of technological applications they are used in - on the other. Additional advantage arises from the unique behavior of the metal/oxide contact interface at the atomic level [1].

## 2 EXPERIMENTAL

To avoid the uncontrollable effect of extrinsic specie the metal/oxide supported structures were controllably formed in ultra-high vacuum conditions (base pressure:  $4 \times 10^{-10}$  mbar) and characterized by a set of complementary surface sensitive techniques: AES, XPS, EELS, LEIS, HREELS, LEED. For AES a double pass cylindrical mirror analyzer with coaxial gun operating at a primary energy of 3 keV and beam current of 10 mA was used. Electron energy loss spectra and LEED patterns were observed by means of retarding hemispherical rear-view four-grid system with normal incidence gun. The work function change ( $\Delta\phi$ ) was measured by Anderson method. The properties of the probing NO molecules adsorbed on the surface of metal deposits have been studied by RAIRS. The latter was carried out using a conventional Fourier-transform infrared spectrometer. The infrared light was introduced into the UHV chamber through CaF<sub>2</sub> window at an incidence angle of about 80 degrees. The absorption spectrum was typically averaged over 300 scans at a resolution of 4 cm<sup>-1</sup>. For HREELS an Ibach type double pass spectrometer (HIB 1000, VSW Scientific Instruments) with monochromatized electron beam was used. Most spectra were collected in a specular direction at a scattering angle of 60° with respect to the surface normal and at incident beam energy of 6 eV. The typical resolution (full width at half maximum) of the elastic peak was about 60 cm<sup>-1</sup>. Thin alumina and magnesia films were prepared by a well-known procedure of

exposing the substrate (Mo(110)) at room temperature to Al and Mg vapor, respectively, in a controlled oxygen atmosphere. Subsequently the films were annealed in an oxygen ambient at 1200 K for Al<sub>2</sub>O<sub>3</sub> and 900 K for MgO. According to the LEED results the oxide films grown in this way exhibit hexagonal structure, at least at a coverage exceeding two monolayers. This corresponds to the structure resembling either  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>(111) or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(1000), and MgO(111). The polar MgO(111) ultrathin film structure, normally unstable for bulk crystal, is formed due to the ordering influence of the Mo(110) substrate and holds up to six monolayers of magnesia. Titanium oxide film was formed via well-known procedure of reactive thermal evaporation of metallic Ti in an oxygen ambient at partial pressure of 10<sup>-7</sup> mbar with subsequent thermal treatment. Metal films were deposited on the formed oxide layers by controlled thermal evaporation via the Knudsen cell. Some other details are presented elsewhere [3,4].

### 3 RESULTS AND DISCUSSION

During the growth of aluminium, magnesium and titanium oxide films on Mo(110), beginning from the submonolayer coverage, the work function gradually

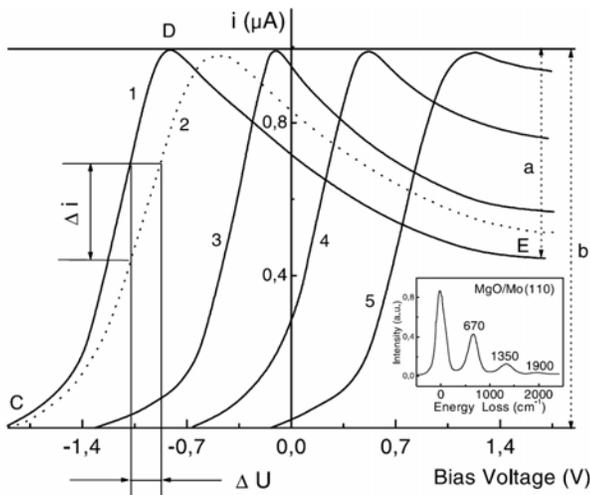


Figure 1: A series of retarding curves for deposition of Cu onto MgO(111) film on Mo(110) at different coverage ( $\theta$ ) of Cu;  $\theta$ , ML: 3-0.4; 4-0.6 and 5-1.1. Curves 1 and 2 correspond to the bare MgO surface at film thickness of 1.5 and 10 nm, respectively. In an inlay a HREELS spectrum of MgO film at a thickness of 1.5 nm, consisting of fundamental and multiple optical phonon losses, is shown.

decreases in all cases until the oxide film coverage becomes equivalent to two monolayers of oxides, after which the work function stabilizes. The stationary values are 3.90 eV, 3.55 eV and 4.1 eV for Al<sub>2</sub>O<sub>3</sub>, MgO and TiO<sub>2</sub>, respectively. At a coverage higher than two monolayers the Auger and HREEL spectra closely resemble those

characteristic for the bulk oxide crystals. As an example, in an inlay of Fig. 1 the HREEL spectrum of MgO film is shown. The one-to-one stoichiometry of MgO film is confirmed by the appearance of sharp optical phonon losses, a characteristic loss pattern for single crystal MgO [5]. Moreover, the shape of the corresponding retarding

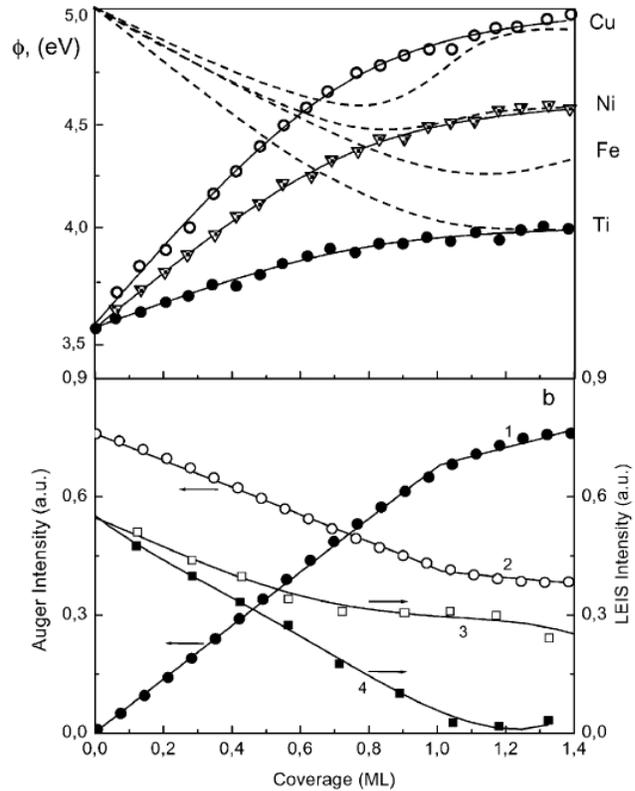


Figure 2: (a) Work function versus coverage plots for Ti, Fe, Ni, Cu on MgO(111)/Mo(110) and Mo(110) (dashed lines). (b) Auger uptake curves of Fe(LVV, 702 eV) (1) and O(KVV, 503 eV) (2) for Fe deposition on MgO(111)/Mo(110) and oxygen LEIS intensity (410 eV) for Cu (3) and Ti (4) on Al<sub>2</sub>O<sub>3</sub>. In all cases substrate temperature during metal deposition is 85 K.

curves in Anderson method might indicate that the oxide films exhibit insulating properties. As an example in Fig. 1 (curve 1), the retarding curve for MgO/Mo(110) is shown, featuring decrease of the current through the sample, covered by oxide film, as the bias voltage sweeps over the so called 'cut-off' point D (part DE). Additional information on the properties of the oxide films can be obtained by comparison of the values of the work function and the coefficient of elastic low energy electron reflection ( $r$ ) of the films and respective bulk crystals. The latter can be defined in the present case as  $r = a/b$  (Fig. 1). The values of  $\phi$  and  $r$  depend on the structure and stoichiometry of the samples, therefore such a comparison may not provide as

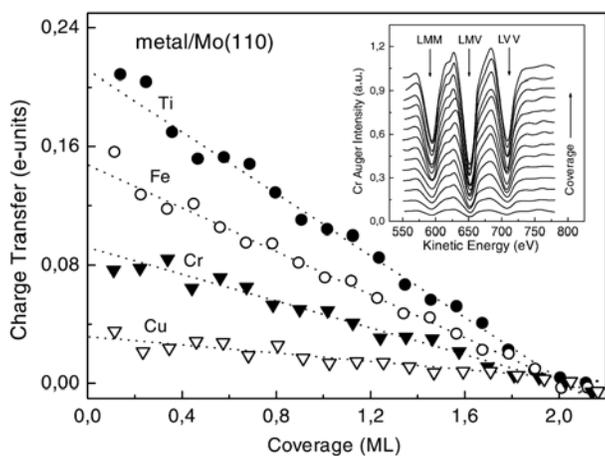


Fig. 3. Charge transfer ( $Dq$ ) versus coverage plots for Ti, Cr, Fe and Ni adsorption on Mo(110) surface. In an inlay a series of Cr Auger spectra in LVV-LMM region at Cr coverage ranging from 0.05 to 2 ML is shown.

straightforward information as that given by AES and HREELS. Nevertheless, a rough agreement of these values measured for the films ( $r = 0.5$ ,  $\phi = 3.55$  eV for MgO,  $r = 0.30$ ,  $\phi = 4.10$  eV for  $\text{TiO}_2$  and  $r = 0.35$ ,  $\phi = 3.9$  eV for  $\text{Al}_2\text{O}_3$ ) with those, reported in the literature for bulk oxides, supports the above assumption that the properties of ultrathin films resemble those of the bulk materials.

For all the metals deposited on oxide films the work function gradually increases until saturation at a coverage close to unity. As an example, in Fig. 2(a) there are work function versus coverage plots for depositing of Ti, Fe, Ni and Cu atoms onto MgO(111) film. For comparison the corresponding plots for the same metals on Mo(110) are also shown (dashed lines). It is seen that  $\phi(\theta)$  plots for oxide and Mo(110) substrates exhibit markedly different trends: In the first case the work function increases, whereas in the latter case the work function decreases. Also the dipole moments of adatoms estimated from the initial slopes of work function versus coverage plots by Helmholtz equation  $\Delta\phi = 4\pi\theta e$  on metal and oxide substrates are markedly different. Such difference might be attributed to quite different electronic state of adatoms at low coverage on the metal and oxide surfaces. As the metal coverage increases the dipole moments gradually change and acquire the value close to zero for all adsorbates and substrates studied at a coverage close to unity. Also, there is a common feature that for both types of substrates (oxides and Mo(110)) the work function at a metal coverage higher than unity has about the same value: 3.9, 4.25, 4.35, 4.6 and 4.9 eV for Ti, Cr, Fe, Ni, Cu, respectively. This may serve as an evidence that at very low metal coverage the properties of the films adsorbed on the oxide and Mo(110) surface are quite different, whereas at higher coverage (close or more than unity) the properties are similar. The growth mode of metal overlayers has been evaluated from the well-known procedure of analysis of the corresponding

Auger uptake curves [6]. An observed linear change of the plots accompanied by a break indicates that the layer-by-layer growth mode occurs, at least up to 1.4 ML. LEIS results corroborate this conclusion: in all cases, except Cu on  $\text{Al}_2\text{O}_3$ , the metal LEIS intensity versus coverage linearly decreases until the value close to zero is obtained at the unity coverage. Such behavior indicates of the complete monolayer formation. As an example, in Fig. 2(b) there are LEIS intensity versus coverage plots of Cu and Ti on  $\text{Al}_2\text{O}_3$  film (curves 3 and 4). Thus, most of the metals studied wet the oxide surfaces.

For comparison of the electronic state of metal adatoms on the oxide films and the Mo(110) crystal, apart from the above measurement of the work function and the dipole moment, we also measured the plots of the metal LVV/LMM Auger intensity ( $I$ ) ratio versus the metal coverage. The LVV Auger intensity is sensitive to the electronic charge ( $q$ ) at the valence level of the metal atom. It was shown that for the first-row transition metals the following relationship holds [7]:  $R = I(\text{LVV})/I(\text{LMM}) = Cq(q - 1)$ . When the metal adsorbs on the substrate surface the value of electronic charge ( $q$ ) at the valence level may

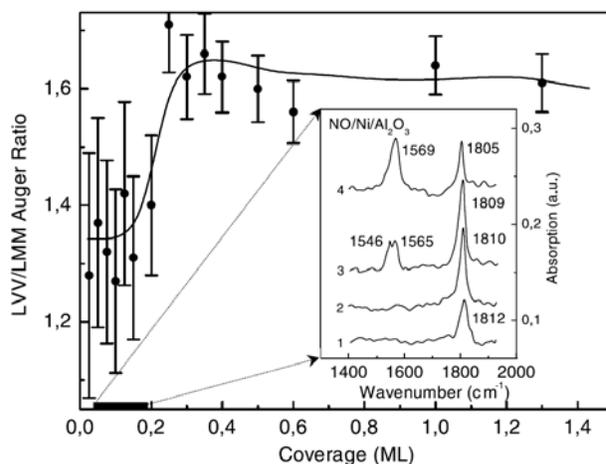


Fig. 4. Fe LVV to LMM Auger intensity ratio versus Fe coverage on MgO(111)/Mo(110). In an inset a RAIRS spectra for NO molecules adsorbed on Ni film on  $\text{Al}_2\text{O}_3$  at different Ni coverage are shown;  $\theta$  (Ni), ML: 1-0.01; 2-0.04; 3-0.1 and 4-0.16. Substrate temperature: 85 K.

change, by the value of charge transfer  $\Delta q$ , due to the formation of chemisorption bonds. In this case, the above equation should be written in the following form:  $R = C(q + \Delta q)(q + \Delta q - 1)$ . The  $\Delta q$  versus coverage plots for Ti, Cr, Fe, Cu on Mo(110) are shown in Fig. 3. As an example in an inlay the Auger spectra of Cr on Mo(110) at a Cr coverage ranging from 0.05 to 2 ML are also shown. It is seen that in all cases the  $\Delta q$  gradually decreases with increasing adsorbate coverage until a value close to zero is obtained at a coverage around 2 ML. The sign of  $\Delta q$  indicates that there is an electronic charge transfer from

adatom to the substrate, and the amount of this charge transfer decreases in the sequence Ti-Fe-Cr-Cu. By extrapolating these plots to zero coverage it is possible to estimate the charges of single adsorbed atoms on Mo(110) surface. These are (in electronic charge units): +0.2, +0.15, +0.1 and +0.05 for Ti, Fe, Cr and Cu, respectively. As the coverage grows, these values decrease (Fig. 3) due to competition of forming lateral metal/metal bonds with metal/substrate bonds.

Unlike Mo(110), adsorption of metal atoms on oxide supports exhibits quite different behavior in terms of adatom to substrate charge transfer. As an example,  $R(\theta)$  plot for Fe on MgO(111) is shown in Fig. 4. With increasing coverage, at  $\theta=0.15$  ML the Auger ratio abruptly increases from the value of 1.3 to 1.6, and does not significantly change as the coverage grows further. This implies that at low coverage (lower than 0.15 ML) the valence electronic charge of the metal is shifted towards the oxide. This assumption is supported by the RAIRS data. In an inset of Fig. 4 there are vibrational spectra of NO molecules adsorbed on the Ni film deposited onto  $Al_2O_3$  surface at low Ni coverages. All spectra correspond to the saturation coverage of NO:  $10^{-6}$  Torr x s. Initially, at a Ni coverage of 0.01 ML a vibrational band at wavenumber  $1812\text{ cm}^{-1}$  appears (curve 1). With increasing  $\theta$  to 0.04 ML the intensity of this line grows with a slight red shift (curve 2). At a Ni coverage of 0.1 ML further increase of the high-frequency band intensity is accompanied by the appearance of a splitted band at a lower frequency ( $1546\text{-}1565\text{ cm}^{-1}$ ) (curve 3). As Ni coverage reaches 0.16 ML the high-frequency line intensity is lowered whereas that of the low-frequency band increases (curve 4). At higher coverage the high-frequency band totally disappears, and only the low-frequency band is evident in the spectrum. The latter resembles the line apparent for NO adsorbed on the bulk Ni crystal [8], and thus may be attributed to NO adsorbed on the Ni islands formed on an oxide. In this regard, it is reasonable to expect that these islands may have adsorptive properties close to those of the bulk metal. The high-frequency band can be explained if one assumes a limited, compared to that of bulk Ni, backdonation from Ni valence orbitals to NO  $2\pi^*$  molecular antibonding orbital. Therefore, it is reasonable to expect that there will be a lack of electronic charge at the valence level of adsorbed metal atoms at a very low coverage compared to the bulk metal. This lack of charge can be reconciled assuming the charge transfer from the metal orbital to the oxide occurring upon chemisorption. Thus, both the LVV/LMM Auger intensity ratio and RAIRS data point at the significant charge transfer from the metal to the oxide at low metal coverage (lower than 0.15 ML). The same trend also holds for metals on Mo(110) surface. However, unlike the metallic substrate, for which the charge transfer gradually decreases with increasing metal coverage and stabilizes at  $\theta > 2$  ML (Fig. 3), for oxides there is an abrupt decrease of the adatom charge at a coverage of 0.15 - 0.20 ML to the stationary value

characteristic for metallic adsorbate. This implies that at low coverage the metal adatoms are ionic (likely with a fractional charge). As the coverage increases, adatoms begin to combine with each other and/or the very small cluster size increases, so that the lateral bonds between adatoms form and the clusters acquire metallic properties manifesting themselves at the coverage higher than 0.15-0.20 ML. Thus, on the oxides, unlike the metal substrate, there is a critical coverage (0.15 - 0.20 ML) separating ionic and metallic adsorption.

## 4 CONCLUSION

Metal atoms adsorbed on the metal crystal on one hand, and the oxide support – on the other, exhibit significantly different properties at very low coverage (lower than 0.15 monolayers), when the metal overlayer can be viewed as consisting of single adatoms and/or very small clusters. This is due to considerably different nature of adatom/support interface interaction at the atomic level. At higher coverage, and especially at monolayer thickness, the metal overlayer has basically the same properties regardless, whether it is supported on the metal or the oxide. Thus, metal/oxide structures at varying metal concentration allow tuning the properties of potentially new devices based on such heterostructures.

## 5 ACKNOWLEDGEMENTS

The reported study was funded by Russian Fund for Basic Research (RFBR) according to research projects # 16-02-00138-a and 16-29-06117-ofi-m. The work has been carried out using equipment of Center of Collective Use of North-Ossetian State University (CKP SOGU) “The Physics and Technology of Nanostructures” with technical support provided within Goszadanie SOGU of Russian Ministry of Education and Science (project # 1772). The work was partly done within FTP NCIMM (STU), PNIER, unique ID RFMEFI57715X0196.

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