

Nickel Nanoparticle Size and Morfology as a Key to Control the Particle Photoluminescence and Photochemistry

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ABSTRACT

Behavior of NO molecules adsorbed on the surface of Ni overlayer deposited on the aluminium oxide film induced by ultraviolet photons generated by nanosecond-pulsed laser at low fluence (3 mJ/cm^2) has been investigated by reflection-absorption infrared spectroscopy (RAIRS) and time-of-flight (TOF) measurements. It is found that in adsorption of NO on Ni/Al₂O₃ at very low Ni coverage (0.04 ML), when the film can be viewed as consisting of separated single adsorbed atoms or very small clusters, the photon irradiation leads to NO desorption. Photodesorption is an essentially non-thermal process, since the mean translational temperature of the desorbing molecules (1100 K) is much higher than the substrate temperature, even with the account of the transient temperature jump caused by the photon crystal.

Keywords: oxide film, nitric oxide adsorption, photodesorption, infrared spectroscopy, time-of-flight spectroscopy

1 INTRODUCTION

In recent years much attention has been devoted to the investigation of reactions of molecules on solid surfaces induced by ultraviolet (UV) and visible photons [1]. Among the systems under investigation the most extensively studied are those formed by adsorption of simple molecules, like CO, NO, NH₃, CH₄, SO₂ and others, on the bulk metal and semiconductor surfaces. The dominant reactions in these systems are desorption and dissociation of the adsorbed molecules. The state-selective detection of desorbing molecules allows to get an insight into the fundamental mechanism of dynamical behaviour of adsorbed species [2]. Despite of the extensive research undertaken in this field, the knowledge about the underlying physics of interaction of photons with adsorbate system is still lacking. In this sense, to promote further understanding of the phenomena, apart from the bulk substrates, the nanosized metal particles and ultrathin films used as a substrates, can be useful. The motivation is that such substrates can have the properties different from those exhibited by the corresponding bulk materials. In relation to this, the aim of the present study is to find out the

mechanism of photochemical behaviour of aluminium oxide supported nickel nanoparticles upon interaction with nanosecond pulsed ultraviolet interaction of UV photons generated by nanosecond pulsed ultraviolet laser.

2 EXPERIMENTAL

The measurements have been carried out in UHV chamber (base pressure: 2×10^{-10} Torr) by means of reflection-absorption infrared spectroscopy (RAIRS), high-resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES). The Mo(110) was chosen as a substrate for aluminium oxide film growth since its lattice constant (2.73 \AA) matches closely with the in-plane O₂- lattice constant (2.77 \AA) of single crystal Al₂O₃. This favours formation of the alumina overlayer with the hexagonal symmetry, possibly α -Al₂O₃ (111) or α -Al₂O₃ (100) [3]. The aluminium oxide film thickness was estimated by AES and was in the 15-20 \AA range. The Ni was deposited on top of the alumina film by thermal evaporation at a growth rate of about 0.005 ML/min. Prior to Ni deposition the substrate was cooled down to 80 K. The NO dose was achieved by backfilling the chamber with NO. The NO dose and subsequent RAIRS and time-of-flight (TOF) measurements were carried out at a sample temperature of 80 K. To stimulate photoreaction in the NO/Ni/Al₂O₃ system the latter was irradiated by ultraviolet light. The UV light ($\lambda=193 \text{ nm}$, photon energy: 6.4 eV) generated from an eximer laser (Lamda Physik, pulse duration 11 ns) was linearly polarised and introduced into the UHV chamber. A $2 \times 2 \text{ mm}^2$ area of the sample was typically irradiated at incidence angle of 30° from the surface normal. The temperature rise of the sample is expected to be lower than 20 K at the fluence used in this experiment (3 mJ/cm^2), and thus thermal effects can be ignored in all measurements. A YAG-pumped tuneable coumarin 450 dye laser (Spectra-Physics, Quanta-Ray PDL-3, line width: 0.07 cm^{-1} , pulse duration: 6 ns) was frequency-doubled by a β -barium borate crystal to probe the desorbing NO molecules.

3 RESULTS AND DISCUSSION

The stoichiometry of the oxide film before depositing Ni was checked by HREELS and AES. The EEL and the

Auger spectrum of the aluminium oxide film of a thickness of about 20 Å grown on Mo(110) are shown in Fig. 1. Following the interpretation proposed by Strong et al [4], the observed loss bands originate from the out-of-phase motion between the in-phase surface and subsurface Al-O layers (400 cm^{-1}), the out-of-phase motion of the surface Al-O species (610 cm^{-1}), and the subsurface Al-O species (885 cm^{-1}). The part of the aluminium oxide film Auger spectrum corresponding to Al-O interatomic transitions is shown in an inset of Fig. 1. This part of spectrum is very sensitive to the oxidation state of Al. As it is seen, there is no sign of metallic Al in the spectrum. Moreover, the peak positions and the relative intensities of A, B and C transitions closely resemble those reported previously for the bulk sapphire crystal [5].

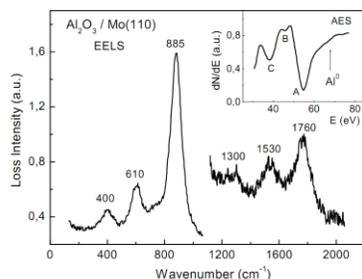


Fig. 1. Electron energy loss and Auger (inset) spectra of 20 Å thick aluminium oxide film grown on Mo(110). Peaks in EELS are due to optical phonon losses, and the peaks A,B,C in the AES are attributed to interatomic Al (L23)-O(V) transitions. No sign of metallic Al Auger transition at 68 eV is observed.

After the oxide film is formed the sample was cooled down to 80 K at which Ni atoms were deposited. According to AES uptake curves the Ni film at this substrate temperature forms a complete monolayer, whereas at RT the 3D-islands of Ni are formed on top of the aluminium oxide thin film. The Ni LMM Auger spectrum at 0.04 ML of Ni deposited on Al_2O_3 at 80 K is shown in Fig. 2 (curve 1). After annealing for 3 min at 400 K the spectrum changes to the form represented by curve 2 (Fig. 2). This change can be explained assuming that annealing leads to the formation of the Ni 3D-islands from the separate Ni adatoms and/or very small particles randomly spread over the surface at 80 K. As such islands are formed the Ni Auger intensity decreases (Fig. 2, curve 2). Likewise, the Auger energy increases due to the final state effects: Extraatomic relaxation energy is higher for the larger metallic clusters on dielectric film [2] leading to the increase of the energy of the ejected Auger electron upon 3D-island formation. The latter, along with the above EELS and AES results (Fig. 1), can be considered as an additional manifestation of the dielectric nature of the underlying aluminium oxide film.

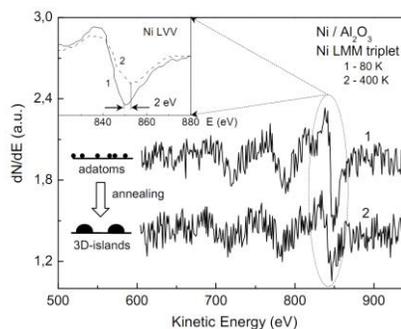


Fig. 2. Ni LVV Auger spectra for 0.04 ML of Ni deposited on top of the 20 Å thick aluminium oxide film at 80 K (1) and after annealing of the formed layer at 400 K (2). Decrease of the Auger intensity and corresponding Auger energy shift (inset) upon annealing imply formation of Ni 3D-islands.

The Ni film at a coverage of 0.04 ML formed at a substrate temperature of 80 K was exposed to NO at an exposure of 10 L ($1\text{L}=10^{-6}\text{ Torr}\times\text{s}$). The corresponding IR spectrum in the NO intramolecular stretch region is shown in Fig. 3a (curve 1). A one absorption band at a wavenumber of 1816 cm^{-1} is apparent. This line is attributed to NO bound to single and/or very small Ni particles modified by the oxide oxygen species. When the system corresponding to curve 1 (Fig. 3) is exposed to UV photons the intensity of the IR line gradually decreases and red shifts with increasing the irradiation time (curves 2-4). Fig. 3, inset, shows a time-of-flight spectrum (points) of NO desorbed from $\text{Ni}/\text{Al}_2\text{O}_3$ corresponding to $v=0, J=1/2-9/2, \Omega=1/2$ states at $\lambda=193\text{ nm}$. The solid curve is the fit to a non-Maxwellian distribution $I(s)=s^3 \exp(-as^2-bs-c)$, where s is the velocity of the molecule and a, b and c are fit parameters. Mean translational energy ($\langle E_t \rangle$) is obtained from numerical calculation and the mean translational temperature is defined by $T_t = \langle E_t \rangle / 2k_B$. The mean translational temperature at the indicated J states is about 1100 K for NO desorbed from Ni particles. The IR spectrum of NO adsorbed on 0.04 ML Ni coverage deposited on Al_2O_3 at 80 K (Fig. 3a, curve 1) dramatically changes when the corresponding system is annealed at 250 K. At this temperature the high - frequency band at 1812 cm^{-1} totally disappears and a new broadened line of a lower intensity centered around 1570 cm^{-1} appears. When the latter system is exposed to UV photons the corresponding IR spectrum does not change even for the prolonged time of laser irradiation, implying complete photochemical inactivity. One can expect that upon annealing the mobility of the Ni species adsorbed on Al_2O_3 at 80 K increases so they coalesce into the 3D-islands similar to the situation represented by Fig. 2. The formed islands might have a bulk-like Ni electronic properties, so that the corresponding NO IR line is located in the spectral range characteristic for NO on different faces of Ni: $1400-1600\text{ cm}^{-1}$. In this sense the photochemistry of NO on such

clusters resemble that exhibited by NO on the bulk Ni crystal in which case no photodesorption stimulated by nanosecond UV laser pulses has been reported. Therefore, it is reasonable to expect that photodesorption occurs only from a single and/or very small Ni particles on the Al_2O_3 film. This situation is realised when a very small amount of Ni (≤ 0.05 ML) is deposited on the substrate surface at low temperature to prevent surface diffusion, and thus formation of 3D-islands.

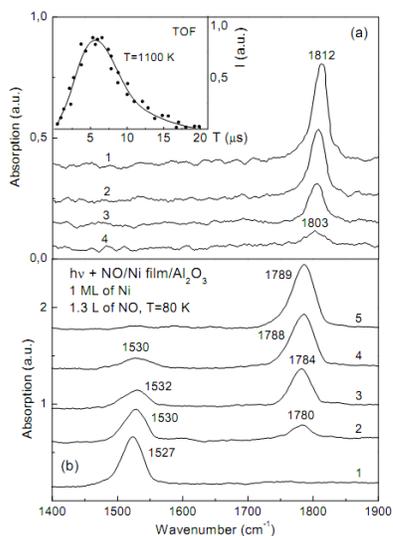


Fig. 3. (a) IR spectra of NO adsorbed on Ni at a coverage of 0.04 ML deposited on alumina film at 80 K before (1) and after (2,3,4) laser irradiation for 3, 6 and 10 min, respectively. IR intensity decrease is due to the desorption of NO, of which evidence is the corresponding time-of-flight spectrum (inset). (b) IR spectra of NO on 1 ML of Ni on alumina before (1) and after (2,3,4,5) laser irradiation for 3, 6, 9 and 15 min, respectively. Transformation of the spectra is attributed to the dissociation of NO.

As it is mentioned above, the high-frequency NO species on Ni monolayer on Al_2O_3 are more stable to laser irradiation than those on Ni(111) bulk crystal: In the former case about two hours of laser irradiation are necessary to decrease the intensity of the corresponding line (Fig. 3b, curve 5) by twice, whereas in the latter case the high-frequency line totally disappears after about 40 min of laser irradiation at the same conditions. To account for this difference one can refer to the known fact that for dissociation to proceed efficiently the adsorption sites to accommodate the dissociation products should be present on the surface [4]. In the case of NO on Ni(111) this requirement manifests itself in that the saturated NO layer is totally inactive to laser irradiation. Photodissociation proceeds only if the layer is not saturated, that is the free accommodation sites are available on the surface [5]. Likewise, when saturated NO/Ni(111) formed at 80 K is heated above 300 K, initially a part of NO molecules should

be desorbed in order to free the accommodation sites for the subsequent dissociation products [3]. Comparing the well-ordered Ni(111) surface and the amorphous thermodynamically unstable Ni monolayer film formed on the oxide surface, one can expect that the density of energetically favourable accommodation sites is higher for Ni(111) than for the amorphous film. Then, it is possible to assume that initially when there are enough free accommodation sites on the monolayer film the dissociation proceeds efficiently mediated by the underlying oxide support (Fig. 3b, curves 1-5). When these sites are being occupied the efficiency of the process is decreasing, so that in order to achieve the situation observed for Ni(111) the prolonged photon exposure is necessary.

4 CONCLUSION

It is shown that nanosecond low-fluence UV-laser induced photochemistry of NO molecules adsorbed on the surface of single and/or very small Ni particles deposited onto aluminium oxide film grown on Mo(110) is markedly different from that observed for NO on bulk Ni(111). In the former case photodesorption channel is operative whereas in the latter case exclusively dissociation occurs. For intermediate Ni coverages when 3D-islands and/or 2D-monolayer are formed the reaction pathway changes from desorption to dissociation. The cross-section of the initial NO photodissociation process in the oxide supported Ni overlayer is noticeably enhanced compared with NO on bulk Ni(111); subsequently the site blocking effect preventing the photodissociation products to be accommodated on the surface reduces the efficiency of the process.

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