TITLE: MOLECULAR ANALYSIS OF TURKISH ALYSSUM L. (BRASSICACEAE) SPECIES BY RAPD-PCR AND SDS-PAGE METHODS

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# ADSORPTION OF Ni AND ITS INTERACTION WITH CsCl MOLECULES ON THE GRAPHITE MONOLAYER OF IRIDIUM

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## ABSTRACT

Adsorption and desorption of nickel on a passive carrier - graphite monolayer on iridium and its interaction with CsCl molecules are studied. It is found that on this surface nickel exist in two phases: in the form of physisorbed atoms and in close packed islands. It is found the that adsorption of Ni atoms on the 2DGF surface on (111) Ir (at T<1000 K) leads to the formation 3D-islands of these atoms. It is found that CsCl molecules dissociate on the surface of Ni islands. Using this experimentally observed fact, in this paper gives new method for determining the area of metallic islands.

*Key Words: Monolayer, two-dimensional graphite films, CsCl molecules, adsorption, desorption,.*

# Ni' İN YÜZEYE BAĞLANMASI VE İRİDYUMUN TEK TABAKA GRAFİT ÜZERİNDEKİ CsCl MOLEKÜLLERİ İLE ETKİLEŞMESİ

## ÖZET

Iridyum üzerindeki grafit tek tabakalı pasif taşıyıcıda nikelin yüzeye bağlanması, kopması ve CsCl molekülleri ile etkileşmesi incelenmiştir. Bu yüzeyde nikelin iki faz olarak bulunduğu gözlendi. Bu fazlar fiziksel olarak yüzeye bağlanmış atomlar formunda ve sıkı paketlenmiş adacıklardır. Ir T<1000 K'de (111) yönelimindeki 2DGF yüzeyinde Ni atomlarının yüzeye bağlanmasının bu atomların 3D adacıklarının oluşumuna neden olduğu bulundu. Ni adacıklarının üzerinde CsCl moleküllerinin ayrıldığı bulundu. Bu çalışmada deneysel olarak gözlenebilen bu sonuçlar kullanılarak metalik adacıkların alanını hesaplamak için yeni bir yöntem kullanıldı.

*Anahtar Kelimeler: Tek tabaka, iki boyutlu grafit filmler, CsCl molekülleri, yüzeye bağlanma, yüzeyden kopma*

## 1. INTRODUCTION

This paper is a continuation of a series of studies on the adsorption and desorption Ni atoms on two-dimensional graphite films (2DGF) on iridium. There are two directions for which such a study is interesting: industrial heterogeneous catalysis (1-5) and solid-state micro-electronics (2,3).

Due to its valence saturation 2DGF is bonded to a surface only by weak van der Waals forces without electron exchange (6). Valence bond saturation is responsible for specific features in the adsorption processes, occurring on the graphite layer. Indeed, if the quasi level $V'$ of the valence electrons of an ad particle lies below the Fermi level ($V' > \varphi$) then the ad particle maintains electrical neutrality and is coupled to the surface by van der Waals forces only (physisorption). If, however, $V' < \varphi$ then the ad atom is partially charged, image forces are then added to the van der Waals forces. Since the add particles have orbitals that are not used in bonds to the substrate this may enhance lateral interaction between them resulting in the formation in the ad layer of clusters and islands with the particles on the graphite layer in a less perturbed state than those on the metal surface.

Indeed, many molecular gases ($I_2$, $Br_2$, $O_2$, CO, $H_20$) (2,7), a number of molecules ($GeI_2$, $GeI_4$ $ZnI_2$) (3,5) as well as Cu and Au atoms (8) undergo only physisorption of atoms of the basal plane of single crystal graphite. The lifetime of NaCl molecule on 2DGF on iridium at 300K was found to be less than $1 \cdot 10^{-5}$ s (corresponding to physisorption with an energy of activation < 0.5 eV) (9).

Adsorption of CsCl molecules on 2DGF on (III) Ir was studied in detail in Ref. (10). It appears that isolated CsCI molecules can only be physisorbed on graphite surface, since even at room temperature their lifetime in the ad layer is less than 0.01s.

## 2. EXPERIMENTAL

The experiments were carried out in a UHV all metal installation: a magnet mass-spectrometer with a residual pressure $\leq 5 \cdot 10^{-10}$ Torr was used for surface studies by the methods of surface ionization and thermionic emission (11-12). The samples used were directly heated polycrystalline iridium ribbons of dimensions 50x1x0.02 $mm^3$, which were texturized by passing them through an AC current. The metal work function, $\varphi$, of the ribbon was 5.80 eV, which coincides with the value of $\varphi$ for the (III) face of Ir (10).

The Ir foil was covered by a graphite layer at a surface temperature of 1600 K by admission of benzene vapor at a pressure of $10^{-5}$ Torr, until the electron emission reached a high and stable value, indicating a work function in the range 4.3-4.4 eV. It is known (6) that the structure of the carbon-covered surface can vary with the conditions used. Here a two-dimensional graphite film is formed. The graphite /Ir system has been studied extensively (see, Ref. (6, 11-15).

The surface is very stable under most conditions, and its properties are actually unchanged even after exposing the sample to air. The temperature of the emitter was measured with an optical pyrometer. Ni have been deposited on 2DGF on iridium by the resistive method. Fluxes of molecules were supplied to the iridium ribbon from Knudsen cell. The ions or electrons emitted from the ribbon's 4mm long central part were measured by a collector system. Part of the ions entered the mass analyzer through a slit in the collector and were detected at the analyzer exit by means of an ion-electron multiplier. The method of investigating the catalytic activity of the surface of the solid by the dissociation of CsCl molecules (16) offers a number of significant advantages (17). CsCl is the simplest molecule with one breakup channel only. One of the dissociation products, the Cs atom, has a low ionization potential (VCs=3.89 eV), and under conditions where VCs is less than the substrate work function (this requirement is met on the surface of high melting point metals, graphite and many others) each Cs ad atom desorbs from the surface of heated adsorbent as $Cs^+$ ion (the mechanism of ion formation is surface ionization (13,18).

If a beam of CsCl molecules of flux density  strikes the surface of a solid  and the products of dissociation and undissolved molecules with density $\nu_{CsCl}$ escape rapidly, then the degree of dissociation $\gamma = (\nu - \nu_{CsCl})/\nu$ will be a measure of catalytic activity in question. Measuring under conditions of complete ionization ($V_{Cs}<\varphi$) the current density of the $Cs^+$ ions desorbing from the surface yields $\gamma$, since $j = e(\nu - \nu_{CsCl}) = e\nu\gamma$. For the CsCI molecules on many metals (Ir, W, Mo, Re, Pt, Pd, Rh, Re) $\gamma$ =l for T>800 K (18-19). Graphite stands out in its unique catalytic passivity: indeed, one monolayer of graphite on iridium reduces $\gamma$ from 1 to $10^{-3}$-$10^{-6}$ (20-21).

We have shown that CsCl molecules are catalytically dissociated with $\gamma$ =1 on Ni islands as it dissociated on the catalytically active metal surface (20). The product of dissociation (Cs ad atom) must desorb as $Cs^+$, because the work function of Ni is greater than the ionization potential of Cs atom. Using the dissociation of the CsCl we determined relative area of Ni islands on 2DGF on (III) Ir.

Measuring the current density of the Cs+ ions desorbing from surfaces:

Measuring the current density of the $Cs^+$ ions desorbing from surfaces:

(1) (111) Ir ($I_0 = e\nu S_0$),

(2) 2DGF on (111) Ir ($I_0^{//} = e\nu\gamma S_0 = \gamma I_0$),

(3) Ni islands on 2DGF on (111) Ir [$I = e\nu\gamma(S_0 - S^{//}) + e\nu S^{//}$]

One can determine the relative area of the Ni islands. The relative area of the Ni islands $s^{//}$ will be determined as $s^{//} = (I - I_0^{//})/(I_0 - I_0^{//})$. The scheme (for M – metal islands) is presented in Fig.1, where $S_0$ is the area of 2DGF and $S_0^{//}$ is the area of islands on 2DGF on Ir.

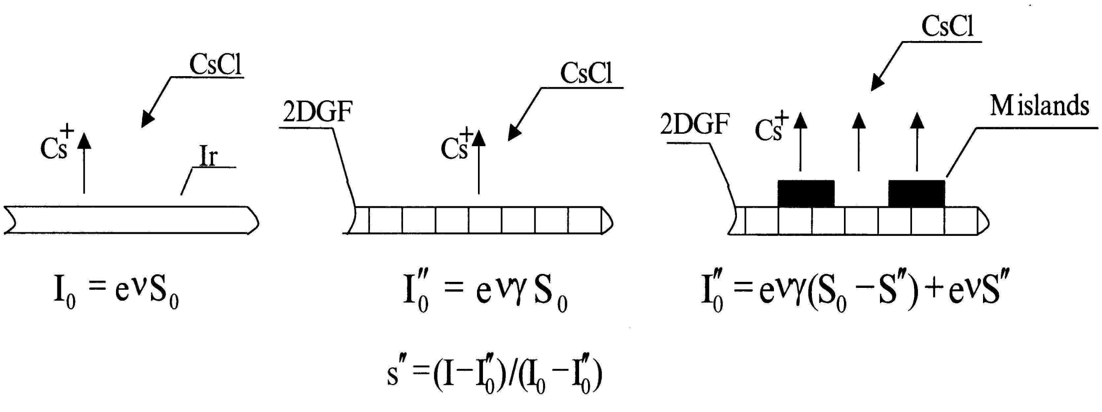

**Figure 1.** The scheme explaining evaluation of relative area of Ni islands on the 2DGF on (111) Ir with use of CsCl molecules adsorption on the surface.

## 3. RESULTS AND DISCUSSIONS

Kinetics of growth of Ni islands:

Ni atoms have been deposited on 2DGF on (111) Ir. One may expect that on the valence-saturated surface of graphite Ni will exist in two phases: in the form of two- (2D) or three-dimensional (3D) close - packed islands and in the form of physisorbed gas similar to Au and Cu atoms on the (001) surface of graphite (8). Due to their high ionization potential Ni add atom on the graphite surface will be in a strengthened state and bonded with surface by weak van der Waals forces.

At T > 1000 K co-adsorption of Ni and CsCl molecules did not lead to an increase in the current due to $Cs^+$ ions: the concentration of Ni ad atoms in the phys sorbed vapour was so small that Ni islands were not created, and the rare meetings of Ni atoms and CsCl molecules in the ad layer did not lead to an increasing Cs+ ion current over the background, coming out from the surface of graphite monolayer while shutting off the Ni atoms flow.

Adsorption of Ni at T < 1000 K lead to formation of Ni islands. It is shown in Fig.2, how the relative area s// of Ni islands increases at different adsorption temperatures T.

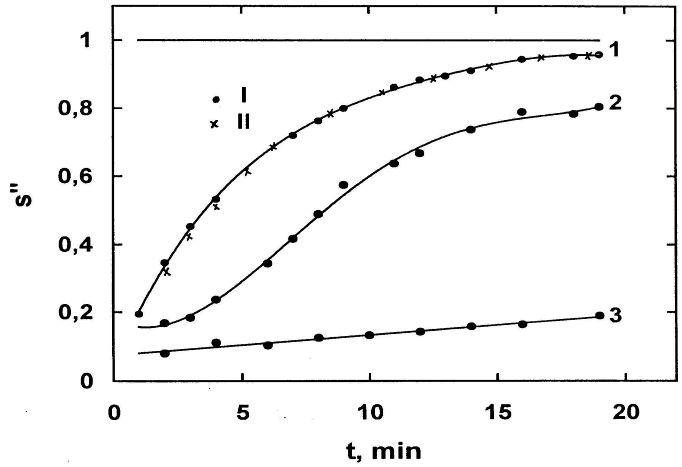

**Figure 2.** Dependence of relative area s//(t) of Ni islands on the deposition time of Ni flow with density Ni = 3 1012cm$^{-2}$s$^{-1}$ onto 2DGF on (111)Ir for different adsorbate temperatures (K): 1-300; 2-580; 3-700. CsCl = 3 1011cm$^{-2}$s$^{-1}$. I-experimental, II - calculation.

A magnitude $s^{//}$ was determined at $T$ = 1140 K. It is seen that with decreasing $T$ the accumulation velocity of Ni in ad layer increases.

Data on the adhesion coefficient of Ni to the graphite monolayer can be obtained from Fig.3. At different temperatures $T$ equal quantities of Ni were deposited onto the surface and values of $s^{//}$ were determined. Two regions exist on the $s^{//}$ (T) dependence: at $T$ > 400 K with decreasing $T$, $s^{//}$(T) increases whereas in the 300 K < $T$ < 400 K region the value of $s^{//}(T)$ is independent of temperature. With decreasing $T$ $\lambda_{Ni}$ increase – a width of migration sink ring, from where Ni ad atoms during their lifetime on the surface gathered to islands (10). If $R$ is radius of the island and $m$ is surface concentration of islands, then Ni ad atoms coalesce to islands from the area

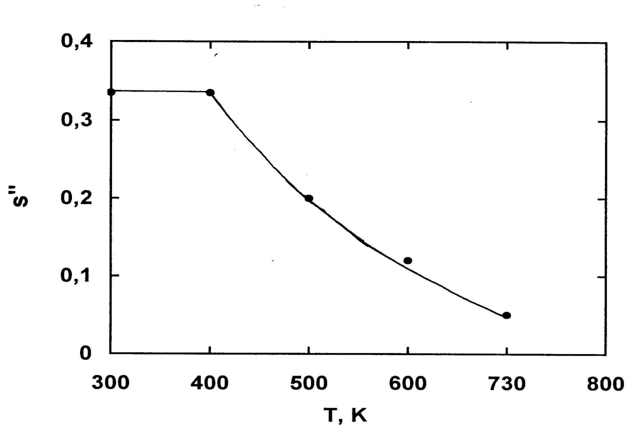

**Figure 3.** Dependence of relative area s//(T) of Ni islands on 2DGF on (111) Ir on adsorbate temperature for equal quantities of Ni deposition.texp = 4 min; Ni = 1.5 1013cm$^{-2}$s$^{-1}$

m[ (R+ M)2 + R2], where M is Ni atom. The absence of the dependence of the collection velocity of Ni atoms in the ad layer on temperature means that the collecting areas of adjacent islands overlap and adhesion coefficient is equal to unity. Such situation also exists in these experiments in the temperature region 300 K< T< 400 K.

Let us analyse which kind of Ni islands (2D or 3D) grow in the afore mentioned experiments. For two-dimensional islands it is necessary that all Ni atoms, dropping on the surface of Ni island, slide down onto the graphite layer (desorption of Ni atoms from the surface of Ni islands can be neglected).

Under the condition of complete slide down and hence, increasing 2D-islands Nmds///dt = M and area of islands must grow linearly in time:

$$s^{//} = \nu_{M} \cdot t \,/\, N_m , \qquad [1]$$

where M is the flux density of M atoms and Nm is the monolayer concentration in Ni islands. If the slide down from islands is absent and 3D-islands grow, then

$$N_m ds^{//}/dt = (1 - s^{//})\nu_M , \qquad s^{//} = 1 - \exp(-\nu_M \cdot t / N_m) \qquad [2]$$

The experimental dependence of s//(t) is essentially non-linear and will be described by expression [2] which evidenced for the three-dimensional nature of the islands. By the comparison of the experimental dependence s//(t) with that calculated, obtained by using the expression [2], from the condition of best coincidence of curves we have obtained the values of N.

An interesting peculiarity in the Ni ad layer has been found, when islands cover the main part of the graphite surface ($s^{//} \geq 0.8 \div 0.9$). It was shown that further deposition of Ni not only does not increase the dimensions of these islands but leads to a strong decrease up to $s^{//} \approx 0.1$, is illustrated by Fig.4. Coalescing of islands in substrate surface (auto-coalescence) occurring during the annealing of non-equilibrium films, is detected in island nature metallic films on neutral substrates (22).

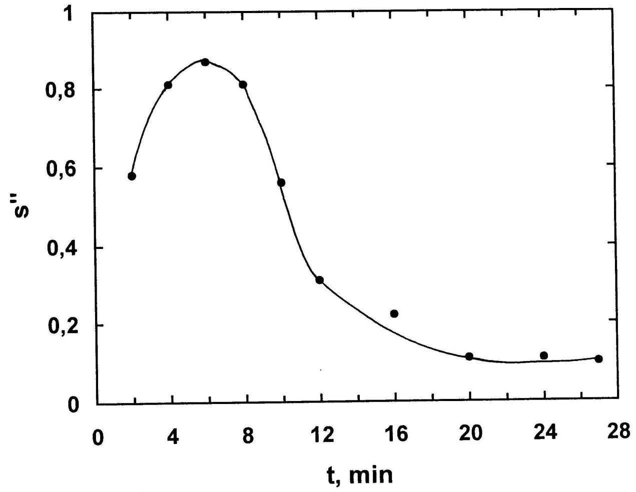

**Figure 4.** Dependence of relative area s//(t) of Ni islands on the deposition time of Ni flow with density Ni = 2.3 1013 cm$^{-2}$s$^{-1}$ onto 2DGF on (111)Ir, holding at temperature 300 K; CsCl = 1.7 1011cm$^{-2}$s$^{-1}$; determining temperature of s//(t) is 1000 K

In Fig. 5 a scheme for variation of the relative area of islands and possible variants of island construction the area decrease are shown.

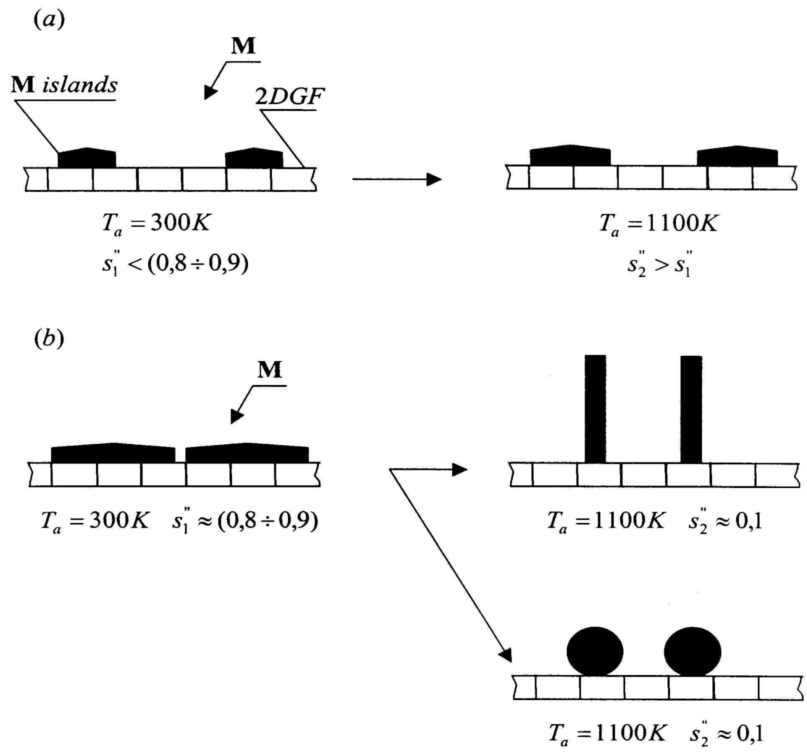

**Figure 5.** The scheme explaining variation of relative area of islands with increasing of temperature (as example, for Pt). Possible variants is shown for creation islands during decrease of their area.

Interaction of CsCl molecules with atoms nickel on the surface of graphite monolayer:

Molecules of CsCl with chemisorbed barium atoms on graphite monolayer enter upon two-stage chemical exchange reaction with products Cs and BaCl (at first stage) and Cs and $BaCl_2$ (at second stage) proceeding in excess molecules CsCl (21). It is interesting to clarity, how chemicals interact with CsCl molecules and Ni atoms. Peculiarities of the system consist in the fact that both reacting particles (CsCl molecules and Ni atom) are weakly bounded with the surface (physadsorption).

Let us estimate the flow of Ni atom $\nu'$, which will come into ad layer with CsCl molecules when flow of these particles supply on the surface. Let us assume that lifetime of Ni atom on graphite monolayer is equal $\tau_{Ni} = 10^{-13} \exp [0.5 \text{ eV}/(kT)]$ (12). Taking into consideration data of (22) let us take lifetime of CsCl molecule on graphite monolayer to be equal $\tau_{CsCl} = 10^{-13} \exp [0.5 \text{ eV}/(kT)]$. Let Ni ad atom is in rest, while CsCl molecules migrate over the surface. Let us take into account that CsCl molecules gathered to point center from the area $S_{CsCl}$ (Å$^2$) $= \pi\lambda^2_{CsCl} = 3.14 \cdot [10 \exp (0.13 \text{ eV}/(kT))]^2$ (10). During the time $\tau_{Ni}$ on the surface 1 cm$^2$ are adsorbed $\nu_{CsCl} \cdot \tau_{Ni}$ molecules of CsCl, which contact with Ni atoms on the part of surface $S_{CsCl} \cdot \nu_{CsCl} \cdot \tau_{Ni} = \delta$, representing probability of Ni atoms meeting CsCl molecules. In this case flow $\nu'$ of Ni atoms, which will come into contact with CsCl on graphite surface, equals to $\nu' = \delta\nu_{Ni} = \pi\lambda^2_{CsCl} \cdot \nu_{CsCl} \cdot \tau_{Ni} \cdot \nu_{Ni}$. Let us estimate flow $\nu'$ under the conditions of these experiment. Let $\nu_{CsCl} = 5 \cdot 10^{11}$ cm$^{-2} \cdot$ s$^{-1}$; $\nu_{Ni} = 3.10^{12}$ cm$^{-2} \cdot$ s$^{-1}$; T = 1000 K. Then $\lambda_{CsCl} = 45$ Å; $S_{CsCl} = 6.4 \cdot 10^{-3}$ Å$^{2;}$ $\tau_{Ni} = 3.3 \cdot 10^{-11}$s; $\delta = 10^{-11}$ and $\nu' = \delta \cdot \nu_{Ni} = 30$ atoms $\cdot$ Ni/(cm$^2$ s).

Thus, only 30 atoms of Ni among the $\nu_{Ni} = 3.10^{12}$ atoms flow, supplying into the surface, will be in contact with CsCl molecules in ad layer.

If non-charged Ni ad atom may come into chemical exchange reaction with CsCl molecules, then extra flow of $Cs^+$ ions of 30 ion/($cm^2 \cdot s$) density will be desorbed from the surface, which is less for many orders of magnitude, than background current of $Cs^+$ ions, going from the surface of graphite monolayer (under the dissociation degree of $\gamma \cong 1 \cdot 10^{-4}$, from the surface are desorbed background flow of $Cs^+$ ions of $\gamma \cdot \nu_{CsCl} = 5 \cdot 10^7$ ion/($cm^2 \cdot$ s) density). In this regard this experiment did not enable us to obtain information on chemical interaction between CsCl molecules physadsorbed on graphite monolayer and Ni atoms. As Ni ad atom is not charged, then data on its chemical interaction with CsCl molecules would elucidate some light on the role of the change of ad particle in its chemical activity- an important problem of the chemistry of surface.

## 4. CONCLUSION

We have studied adsorption and desorption of Ni atoms on the solid-state surface of a graphite monolayer on Ir. In addition co-adsorption of CsCl molecules and Ni atoms on the same surface have been studied. It is found the that adsorption of Ni atoms on the 2DGF surface on (111) Ir (at T<1000 K) leads to the formation 3D-islands of these atoms. It is found that CsCl molecules dissociate on the surface of Ni islands. Using this experimentally observed fact, in this work, was given new method for determining the area of metallic islands.

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