BNL - 67183

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July 1999

National Synchrotron Light Source

Brookhaven National Laboratory
Operated by
Brookhaven Science Associates
Upton, NY 11973

Under Contract with the United States Department of Energy
Contract Number DE-AC02-98CH10886

Diffuse scattering of the conduction electrons of a metallic substrate by an adsorbate : an experimental study using synchrotron infrared radiation.

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ABSTRACT

Due to its intrinsic high brightness, high stability, and proportionality to the stored electron beam current, synchrotron IR spectroscopy has revealed itself as an unique tool to experimentally test a physical phenomenon occurring at metallic interfaces, the theory for which was motivated by previous observations. Any adsorbate induces inelastic scattering of the conduction electrons, which causes a broadband IR reflectance change, and was predicted to induce a concomitant DC resistivity change. By choosing a well ordered single crystal thin film of Cu(111)), we have checked that the DC resistivity change, and the asymptotic limit of the IR reflectance change are linearly dependent, but independent of the nature of the adsorbate. Coadsorption experiments which have been used to modify the induced density of states at the Fermi level, have further demonstrated that the friction coefficient, which is responsible for the elastic scattering phenomenon, is chemically specific.

Keywords: Synchrotron, infrared, friction, Cu(111), thin films, resistivity, coadsorption , scattering.

1. INTRODUCTION

The subject of adsorbate bonding and intermolecular dynamics has attracted considerable attention , with much of the information about the nature of the bond being inferred from measurements of the intramolecular vibrational modes in the 600-4000 cm-1 frequency range[Yates, 1987 #1][Clark, 1988 #2][Chabal, 1988 #3][Dumas, 1999 #4]. Particular emphasis has been paid to adsorbate dynamics involved in electronic and vibrational couplings to the substrate. These couplings also affect the transport properties of the substrate, and, for example, an important change in the resistance of a metal film can be induced by an adsorbed layer [Schumacher, 1993 #5]. This has been experimentally studied in recent years by measuring the DC resistance change induced by various adsorbates [Schumacher, 1993 #5]. It became obvious that an analogy could be drawn between this electrical effect and some new observations in the infrared spectrum of molecules at surfaces [Hirschmugl, 1990 #6] who made the observation that an adsorbed molecule induced the appearance both of an anti-absorption feature, and a broadband reflectance change. By applying the concept of friction to all vibrations of an adsorbate including a component of velocity oscillating parallel to the surface (for instance the frustrated translations and rotations), Persson and Volokitin [Persson, 1991 #7] were able to explain the appearance of antiabsorption bands and the overall lineshape of the broadband reflectance change. The friction coefficient between the sliding adsorbate and the conduction electrons of the metal is a key parameter that can explain both the resistance change of the metallic film and the broadband infrared change. This friction coefficient has been suggested to be inversely proportional to the electronic damping of the parallel vibrational motion. It became therefore of paramount interest to determine accurately this friction coefficient using either the resistance change, or the broadband IR reflectance change, and relate it to a lifetime of the motion. This latter parameter , which is extremely importat in processes like diffusion, reactivity ect., could thus be accessed in a much simpler experimental way.

However, the model which involves the elastic scattering of the conduction electrons of the metal by the adsorbate, has been debated.[Tully, 1993 #10][Germer, 1993 #11][Culver, 1993 #12]. There thus was a clear need for further experiments. It was recognized earlier on that the diffuse scattering of conduction electrons from surfaces necessarily reduces the infrared reflectance of the surface [Holstein, 1952 #13][Dingle, 1953 #14]. Regardless of the lifetime consideration , a linear dependence between the resistance change ΔW of a thin metal film and the asymptotic limit of the IR reflectance change ΔR induced by theses molecules is expected. This relationship was explicitly described by Persson [Persson, 1991 #8] and Lin et al.[Lin, 1993 #15]. First attempts to verify experimentally the linear dependence between the DC resistivity and IR reflectance change were performed for polycrystalline films[Hein, 1995 #16], and for epitaxially grown Cu(100) films[Krastev, 1997 #17]. However, none of these two studies could simultaneously record the broadband reflectance change, the resistivity, and the various vibrational bands (dipole-allowed and dipole-forbidden modes).

For such a purpose, synchrotron infrared spectroscopy at surfaces appears to be unique. On one hand, thanks to the high stability of this source, numerous experiments have been carried out successfully, with high reproducibility, over the frequency range 20-3000 cm-1. On the other hand, the fast recording time of this technique allows the broadband reflectance change to be measured accurately for comparison with the theoretical predictions.

The aim of this work is to verify the validity of the friction model for Cu(111) films grown on TiO_2 substrates by studying simultaneously, the changes induces in the DC resistivity, in the broadband IR reflectance , and in the amplitude and shape of the vibrational features induced by various molecules (CO, ethylene) and atoms (Cs), as a function of the adsorbate coverage. We found a very satisfactory agreement for the elastic scattering model. More importantly, using coadsorption experiments, we have shown that the friction coefficient is dependent on the adsorbate-induced density of states at the Fermi level (E_F), another property that has been predicted theoretically [Persson, 1991 #8].

2. EXPERIMENTAL

A detailed description of the synchrotron infrared reflection-absorption spectroscopy set-up can be found elsewhere[Hein, 1999 #18]. However, it is worth noting that accurate measurements of the broadband IR- reflectance change are far more demanding experimentally than the more common recording of the vibrational spectrum. The main requirements are the high stability of the electron beam position and the high brightness of the infrared source. With a thermal source temperature fluctuations provide considerable uncertainty in the incident beam intensity. On the other hand, synchrotron radiation is an absolute source whose brightness, for a given ring, is determined only by the stored current which can be accurately measured. Some years ago, a global feedback was developed at the National Synchrotron Light Source [Yu, 1989 #19] which greatly improved the long-term stability of the beam and this system continues to be improved.

The broadband IR reflectance and resistance change were acquired simultaneously for Cu (111) films, of various thicknesses, epitaxially grown on a TiO_2 (110) substrate. The substrate was first annealed by resistive heating for 5 hours at 973K. Various copper film thicknesses ranging between 20 to 100 nm were made using slow evaporation rates of $\approx$ 0.1nm/s. After preparation of the 15mm × 10mm film, four 200nm thick copper pads were evaporated onto the edge of the film to allow measurement of the film resistance W. The absolute resistance value was determined with a four terminal method. In order to register small changes ΔW of the film resistance, the film was made part of a Wheatstone bridge which was supplied with alternating current [Hein, 1999 #18]. A lock-in amplifier was used to improve the signal to noise ratio.

The film was sputtered after each exposure, and the loss in film thickness due to this cleaning process was compensated by evaporating additional copper at room temperature until the original resistance of the film was retrieved. After a short annealing at 400K , the LEED pattern confirmed that the films were again of (111)-orientation.

In order to avoid the effects of instabilities, which can result in intensity oscillations within the spectral distribution of the broadband reflectance change, a stringent procedure of data selection was adopted: after the temperature stabilization (as judged by the stability of the film resistance), 5 spectra of 64 scans each, at a resolution of 8 cm^{-1} (17 seconds per spectrum) were recorded. The last spectrum was ratioed to the first, and exposure to CO gas, or to Cs was initiated only if a "flat" baseline was obtained between 180 and 500 cm^{-1} for the bolometer, or 300-3000 cm^{-1} for the Cu: Ge detector .

Exposure to CO was performed by backfilling the chamber, while a doser, facing the sample, was used for the ethylene. For alkali deposition, a thoroughly outgassed Cs getter was used. During alkali deposition, the pressure in the chamber never exceeded $2x\ 10^{-10}$ Torr. For each exposure, the same data selection procedure was followed to make sure that no drift was present, but the number of spectra recorded for each exposure was limited to 3 in order to shorten the recording time. After good quality spectra were recorded, they were individually normalized to the beam current.

3. RESULTS AND DISCUSSION

Figs. 1 and 2 show the typical information that has been obtained from these experiments. In Fig. 1, we show the weak broadband IR reflectance change observed when exposing a Cu(111) thin film (30 nm thick). On top of this figure, the DC resistance change, measured for the same film, is displayed. The total reflectance change amounts to 0.3 ± 0.05 %. This asymptotic limit for the reflectance is found to be less than that obtained for a monolayer of CO (Fig. 2). ($\approx 1.2 \pm 0.2$ %). This is due to the different scattering cross sections of the two different adsorbates, as discussed later..

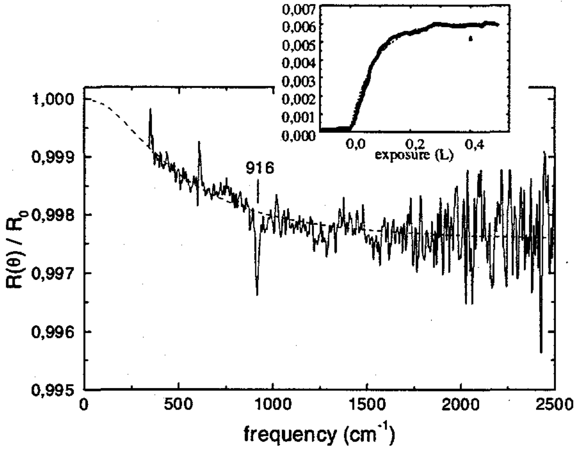


Fig.1: Broadband IR reflectance change for ethylene , at saturation, adsorbed at 90K, on a 30 nm Cu(111) thin film. On top is shown the amplitude and shape of the DC resistance change during exposure to the ethylene.

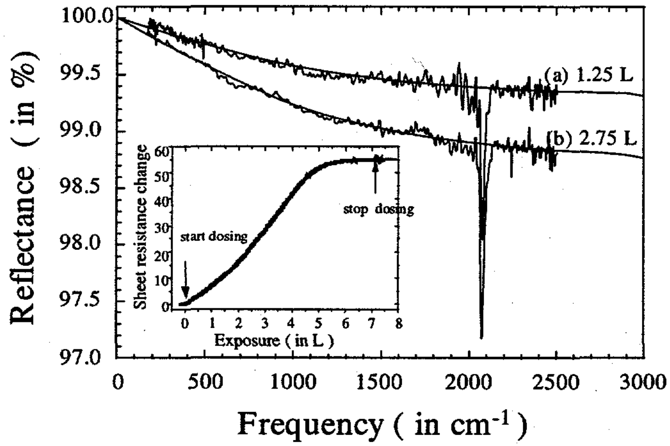


Fig2: Broadband IR reflectance change for CO adsorbed on a Cu(111) film, 67 nm thick, at T=90K. The solid lines through the spectra are fits according to Persson and Volokitin's model [Persson, 1991 #7]. The insert shows the change and shape of the resistance during CO exposure.

In order to analyze the experimental data presented above, we have used a theory based on the concept of "friction" between the adsorbate and the conduction electrons of the metallic substrate[Persson, 1991 #7]. This frictional force depends only on the relative motion between the adsorbate (velocity $\dot{u}$) and the "hydrodynamic" drift velocity $v_{//}$, of the electron "fluid" right below the interface, and parallel to it. The relative motion between the adsorbate and the electron fluid will give rise to a friction or drag-force f on the adsorbate given by:

$$f = -M\eta\left(\dot{u} - v_{//}\right) \qquad \{1\}$$

where M is the mass of the adsorbate, and η the friction coefficient. The lifetime τ of the parallel frustrated vibration of an atomic adsorbate is given by

$$\frac{1}{\tau} = \frac{1}{\tau_{e-h}} + \frac{1}{\tau_{phonons}} \qquad \{2\}$$

and $\eta = 1/\tau_{e-h}$. The microscopic theory of the friction [Persson, 1991 #8] based on the Newns–Anderson model yields:

$$\eta = \frac{\hbar}{M}\Gamma\rho(E_F)\langle k_{//}^2\rangle \qquad \{3\}$$

where Γ is the width of the adsorbate-induced resonance state, $\rho(E_F)$ the induced density of states , and

$$\langle k_{//}^2\rangle = \frac{\sum_k k_{//}^2 |V_{ak}|^2 \delta(E_F - \varepsilon_k)}{\sum_k |V_{ak}|^2 \delta(E_F - \varepsilon_k)} \qquad \{4\}$$

Here, V_{ak} is the electron transfer interaction between the adsorbate orbital $|a>$ and metal state $|k>$,and $k_{//}$ is the wave-vector component parallel to the surface of an electron in the orbital $|k>$.

According to the diffuse scattering model, the friction coefficient can be obtained either from from the asymptotic "high frequency " value of the IR reflectance change:

$$\Delta R_p = -\frac{4}{c}\frac{n_a}{n}\frac{M}{m}\frac{\eta}{\cos\Theta}F \qquad \{5\}$$

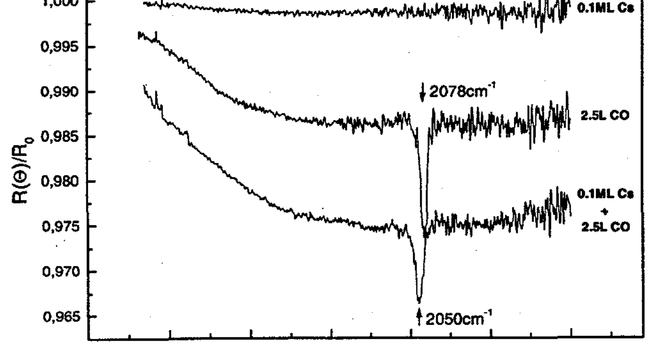
(where F is a correction factor which is important at grazing incidence geometry[Otto, #20]), or from the resistance change:

$$\frac{\Delta W}{n_a} = \frac{M\eta}{(ned)^2} = \frac{M\eta}{(ned)^2} \qquad \{6\}$$

where n , e and d are the number of conduction electrons per unit volume , the electron charge and the film thickness , respectively.

For CO adsorbed on a 42 nm Cu (111) thin film, the initial slope of the resistance change was found to be 2.45×10^{10} $\mu\Omega A^2$, yielding $\eta = 1.73\times10^{10}$ s^{-1}, while the asymptotic (high frequency) limit of the IR reflectance change (1.15% for $n_a = 0.061 A^{-2}$) yields $\eta = 1.23\times10^{10}$ s^{-1}. Accounting for errors associated with the determination on the film thickness (the calculation of the friction coefficient depends on the **square** of the film thicknessfrom Eq.{6}), these values are in satisfactory agreement. This was also verified for ethylene adsorbed on a 33 nm Cu(111) thin film. A value of 5.2×10^9 and 6.4×10^9 s^{-1} are found from the asymptotic limit of the IR reflectance change and the initial slope of the DC resistance change, respectively.

One interesting property of the friction coefficient is its chemical specificity (Eq.{3}). To address this issue experimentally, thorough tests have been carried out using coadsorption experiments. The coadsorption of alkali metals with carbon monoxide on transition metal surfaces has been intensively studied in the past [Bonzel, 1987 #21]. It has been shown that on noble and transition metal substrates, coadsorbed alkali weakens the C-O bond but strengthens the CO-metal bond, thus inducing a marked reduction (downward shift) of the C-O stretch frequency and an increase of the CO-metal binding energy . Two processes have been proposed to account for the frequency shift of CO, namely (a)- a "through metal" or metal mediated (charge flows between nearest neighbor molecules through the metal) interaction , where the alkali metals donate charge to the metal substrate which is partially transferred to the CO $2\pi^*$ orbital [Feibelmann, 1984 #22] , and (b)- a vibrational Stark effect , due to the direct interaction between the electric field of the positively charged alkali atoms and CO[Muller, 1986 #23]. A recent study of the coadsorption of potassium with CO on Cu (111) in the low coverage regime ($\Theta_K = 0.08 - 0.2$), indicates the importance of process (a). Nevertheless, there is no clear conclusion of which mechanism dominates. The effects of charge transfer into the CO $2\pi^*$ orbital and of significant 1π-K(PAUL DO YOU MEAN Cs HERE?) direct interaction can combined to account for the vibrational frequency shift of the adsorbed molecules.



In Fig. 3, we show the infrared spectra for (a) CO and (b) CO/Cs on a thin (60 nm) Cu(111) film.

Fig.3: Infrared spectra of Cs, CO and Cs+CO adsorbed on a 82 nm Cu(111) thin film, at 90K. Note the very weak broadband reflectance change induced by the deposition of 0.1ML of Cs, but the much larger change when coadsorbing the same amount with CO.

For a film predosed with 0.1 ML of Cs, the frequency of the C-O stretch mode is downward shifted by 28 cm-1, and the peak broadens (by about a factor of 2), but keeps its integrated intensity. Interestingly, the broadband IR reflectance change reaches a markedly different asymptotic value (2.2 % instead of 1.15 % for CO/Cu (111)). Taking into account an equivalent adsorbate concentration at saturation, for the CO/Cu (111) and CO/Cs/Cu (111) systems, we conclude that the charge transfer induced by preadsorbed alkali has increased the friction coefficient:from $\eta = 1.23 \text{x} 10^{10}$ s to $\eta = 2.5 \text{x} 10^{10}$ s^{-1}.
A thorough analysis of the dependence of friction coefficient on charge transfer will be published elsewhere [Hein, in preparation #24]. A similar effect has been also observed for the coadsorption of CO and ethylene on Cu (111) thin films, and will be reported in detail elsewhere [Hein, in preparation #24].
These experiments are clearly consistent with the microscopic theory of the friction coefficient based on the Newns-Anderson model .
However, to complete this experimental est of the scattering model ,an important reliationship has to be verified: the linearity between the reflectance change , at the asymptotic limit, and the DC resistance change:

$$\frac{\Delta R_p}{\Delta W} = -\frac{\omega_p^2 . d^2}{\pi . c} . \frac{F}{\cos\Theta} \qquad \{7\}$$

where ω_p and d are the plasma frequency and the thickness of the metallic film, respectively. Equation{7} shows that this linear relationship must be independnent of the adsorbate and on its concentration, and depends only on the nature of the film , and its thickness.
By recording the DC resistance change , and the asymptotic limit of the broadband IR reflectance change induced by various amounts of different adsorbed molecules or atoms, and different coadsorption systems, we have been able to verify that such a linear relationship is obtained, (Fig.4).

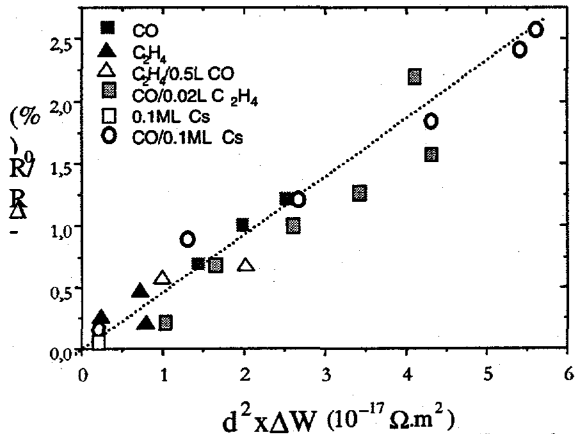


Fig.4: Relationship between the measured asymptotic limit of the reflectance change and the resistivity change of Cu(111) thin films, for various adsorbates (CO, Cs, Ethylene), and various coadsorbate systems (Cs+CO and ethylene +CO) at different coverages. The linearity observed is in line with the model involving the elastic scattering of the conduction electrons of the metallic substrate by the sliding adsorbate.

From the results which have been obtained on the different systems studied, it is evident that we have made a thorough and satisfactory check of the scattering model proposed by Persson et al.[Persson, 1991 #7],[Persson, 1991 #8],[Persson, 1992 #9]. Whether or not this model can be universally applied to all adsorbate-metallic systems still has to be verified. There are some conflicting experiments which show that some observations cannot be accounted for by this model. For example, the adsorption of formic acid on Cu(100) leads to an almost zero-reflectance change [Krastev, 1997 #17].

The most important aspect of this model is that it may provide a more tractable experimental method for determining the lifetime of parallel motions of adsorbates relative to the substrate. Among the questions that can be raised is whether or not this lifetime is purely of electronic origin. Recent determination of the lifetime of the frustrated translation of CO on Cu(100) surface by Helium Atom Scattering [Graham, 1996 #25] and by time resolved infrared experiments [Germer, 1993 #11], set values of 17 and 5 ps respectively. This is approximatively a factor of 10 less than the one extracted from the broadband IR reflectance change, or the slope of the resistivity change.

The experimental checks that have been performed here cannot address issues regarding the contribution of the phonon-phonon couplings in the lifetime of the frustrated motion. However, we have recently shown that one has to consider an additional factor which contributes , at least, to the broadband IR reflectance change: a "geometrical" term.

For CO adsorbed on Cu(110), an anisotropy in the lateral momentum (frustrated translational motion) has been observed [Ahner, 1997 #27]. CO is adsorbed on top sites, so there are have two different momenta either along the <110> or the <001> directions (Fig. 5)

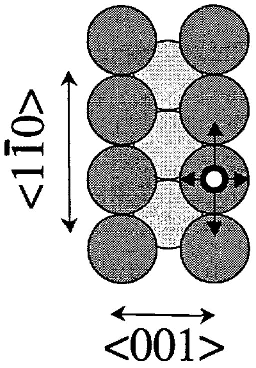


Fig.5: Schematic of CO adsorbed on the anisotropic Cu(110) surface. The arrows show the anisotropy observed by Ahner et al. [Ahner, 1997 #27].

Broadband IR reflectance change can be probed anisotropically on a metal surface using p-polarized light since this produces a field parallel to and beneath the surface in the incidence plane (defined by the incident direction of the impinging beam, and the perperdicular to the surface). A large broadband reflectance change was been observed by C. Hirschmugl et al.??? , with a magnitude almost identical to that oberved for Cu(100) and Cu(111) when the incidence plane was oriented along the <001> direction.

We have recorded the broadband IR reflectance change for CO /Cu(110) by probing along the <110> direction (see Fig. 5). Surprinsingly, no broadband reflectance change is observed (Fig. 6).

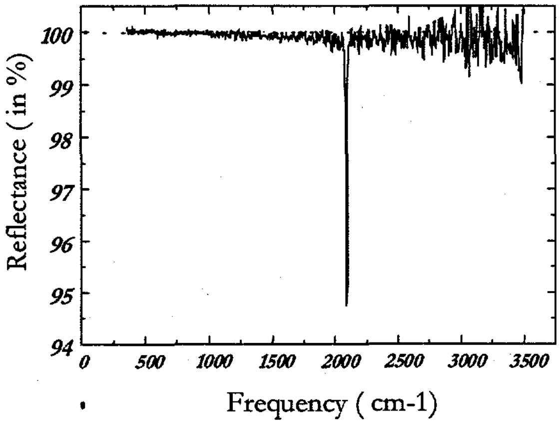


Fig. 6: Broadband reflectance for a saturation coverage of CO on Cu(110) ratioed to the reflectance of clean Cu. The incidence plane was set along the <110> direction. No detectable change was observed, contrary to what was observed in the perpendicular direction [Pilling, To be published #28].

Detailed analysis shows that, accordingly, no frustrated rotation is observed. A thorough analysis of these results are underway [Pilling, To be published #28]. This demonstrates that further considerations have to be taken into account to fully understand the origin and amplitude either of the broadband reflectance, or the DC resistivity changes of monocrystal or thin metallic films.

4. CONCLUSIONS

Synchrotron infrared reflection studies have been carried out, simultaneously with DC resistivity measurements, on thin films of Cu(111) , epitaxially grown on TiO_2 substrates. The amplitudes of the broadband reflectance changes, which can be accurately measured thanks to the proportionality of the infrared intensity to the stored electron current in the ring, were found to be similar to those observed previously on single crystals. (PAUL WHAT DOES THIS MEAN?) →→→→→However, the overall shape of the reflectance change with frequency, was found to be dependent on the thickness of the thin film. This is consistent with the theoretical description made by B.N.J. Persson et al., who suggest that elastic scattering of the conduction electrons of the substrate by the sliding adsorbate (the sliding friction), can fully describe the reflectance change, as well as the appearance of antiabsorption features. Combining those measurements with resistivity on the same film allowed us to perform the first thorough check of this theory. We found a very good agreement with respect to the linearity observed between the amplitude of the IR reflectance change, and the DC resistivity change, for a film of known thickness.

One important assumption has also been verified. The friction coefficient depends of the induced density of states by the adsorbate. By varying this density of states , using coadsorbed CO, Cs and ethylene, we have been able to demonstrate this "chemical" specificity : an increased density of state leads to an increase of the asymptotic limit of the broadband IR reflectance change, and an increase of the DC resistivity change, both quantities remaining linearly related.

This work clearly shows that the PAUL ISN'T IT INELASTIC?? elastic scattering theory is relevant in describing the dynamic interactions between an adsorbate and a free-electron like metallic substrate. . However, recent experiments indicate that for a real surface, additional factors , such as geometrical ones, are imortant.