"standard-state contribution on the *i*th sublattice G°_{ij} " (eq 19). It was stated that "chemical potentials can only be attributed to independently variable components of a phase

$$\mu_{ij} = \left(\frac{\partial A}{\partial N_{ij}}\right)_{N_{gh}(g\neq i,h\neq j),B_i,T}$$
(21)

i.e. while adding ion j to i, we have to keep constant the number of sites and the number of ions in that site or in any other site, which is clearly impossible while preserving electrical neutrality." However, this objection can also be made on the definition of the chemical potential in (6) for a cation in the framework. Barrer¹² stresses that the chemical potential of a cation in association with a framework as defined by Gaines and Thomas¹³ in their original work implies the cation with his electrochemical equivalent of framework, a neutral grouping which does form an independently variable component. However, it can be argued that expression 6 is not a thermodynamic issue: it is a formal thermodynamic defintion and not a process. Guggenheim¹⁴ describes that, in dealing with charged components, one degree of freedom is lost due to the electroneutrality requirement. If we assign in a phase an arbitrary value to the activity (and hence the chemical potential) of one ionic species, the activities of the remaining compounds are unambiguously determined and can be used correctly in the formal treatment of the thermodynamics.

The expression of the chemical potential in section 2 may shed new light on the issue. Equation 7 can be transformed to

$$\mu_{j} = u_{ij} + kT \ln \frac{N_{ij}}{B_{i} - \sum_{i=1}^{m} N_{ij}}$$
(22)

From eq 22, it appears that a chemical potential in a particular group of sites can be defined. However, if we try to give a sublattice with its cation a thermodynamic status by itself, it consequently must satisfy all thermodynamic relations as e.g. the Gibbs-Duhem relation which states (at constant T and P in the sublattice)

$$\sum_{k} N_k \, \mathrm{d}\mu_k = 0 \tag{23}$$

(12) Barrer, R. M. Personal communication, 1989.

(13) Gaines, G. L.; Thomas, H. C. J. Chem. Phys. 1953, 21, 714.

(14) Guggenheim, E. A. *Thermodynamics*; North-Holland Publishing: Amsterdam, 1959; pp 337-349. where the summation is taken for all components k present in the phase.

If we assume that the chemical potential of the negatively charged sublattice does not change with different cationic composition (just as we neither included a partition function of the lattice in eq 4), the summation in eq 23 contains the terms of the cations only. Furthermore, to calculate the total differential of μ_k , eq 22 must be derived with respect to all independent variables. If we consider only variations in composition at constant temperature and constant amount of exchanger, (23) becomes for a sublattice loaded with two types of cations A and B

$$N_{iA}\left\{\left(\frac{\partial\mu_{A}}{\partial N_{iA}}\right)_{B,T,N_{iB}} dN_{iA} + \left(\frac{\partial\mu_{A}}{\partial N_{iB}}\right)_{B,T,N_{iA}} dN_{iB}\right\} + N_{iB}\left\{\left(\frac{\partial\mu_{B}}{\partial N_{iA}}\right)_{B,T,N_{iB}} dN_{iA} + \left(\frac{\partial\mu_{B}}{\partial N_{iB}}\right)_{B,T,N_{iA}} dN_{iB}\right\} = 0 \quad (24)$$

which transforms using (22) to

$$kT\left(\frac{B_{i} - N_{iB}}{B_{i} - N_{iA} - N_{iB}} dN_{iA} + \frac{N_{iA}}{B_{i} - N_{iA} - N_{iB}} dN_{iB}\right) + kT\left(\frac{B_{i} - N_{iA}}{B_{i} - N_{iA} - N_{iB}} dN_{iB} + \frac{N_{iB}}{B_{i} - N_{iA} - N_{iB}} dN_{iA}\right) = 0$$
(25)

Rearranging (25) yields

$$B_i(dN_{iA} + dN_{iB}) = 0$$
 (26)

Since the number of cations on a site is not constant through the exchange process, i.e., dN_{iA} does not necessarily equal dN_{iB} , condition (86) is not satisfied. This is the reason why the assembly of sites *i* cannot constitute a thermodynamic phase by itself and why no selectivity constant can be assigned to this sublattice. Defining a Gibbs phase requires that all components must be able to vary independently (accounting however for the electroneutrality restriction which reduces the number of independent components from k to k - 1 in the phase). The number of one type of cation in a particular group of sites in a zeolite is *not* an independent variable: it is an equilibrium value depending on the total number of cations in the zeolite.

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Decomposition of Tetrahydrofuran on MoS_2 and $Li_x MoS_2$

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Chemisorption and thermal evolution of tetrahydrofuran (THF) on various MoS₂ surfaces were studied by ¹³C CP/MAS NMR spectroscopy. In all cases the adsorption is nondissociative at room temperature. On pure MoS₂, decomposition of the adsorbed layer begins at 150 °C, the initial reaction product being aldehyde. On LiMoS₂, reaction begins at a higher temperature, while on Li₃MoS₂ the initial product is chemisorbed butoxide. At high temperatures, the carbon from THF is converted entirely to small aliphatic hydrocarbons, CO₂, and adsorbed aromatic residues.

Introduction

 MoS_2 is a useful cathode material for rechargable lithium batteries¹ due to its ability to reversibly intercalate lithium within the crystal structure. The chemical potential of the intercalated lithium is so low that a cell voltage of 1.8 V can be obtained under typical operating conditions. One of the practical problems with such cells is decomposition of the organic electrolytes which must be used to dissolve lithium salts in the presence of metallic Li.

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⁽¹⁾ Haering, R. R.; Styles, J. A. R.; Brandt, K. U. S. Patent 4224390, 1980.

Such decomposition shortens the life of the battery and leads to a potential explosion hazard, since the products are at least partially gaseous. Some decomposition undoubtedly occurs on the Li anode and is to some extent controllable by suitable choice of electrolyte. The question remains whether decomposition reactions can also occur at the cathode, which approaches metallic Li in thermodynamic potential, as the cell discharges. Another possibility is catalytic decomposition at the MoS₂ surface; decomposition of THF to water or carbon oxides, plus hydrocarbons, is thermodynamically favorable at ambient temperature. The present work attempts to investigate the possibility of decomposition at the MoS_2 cathode.

In this work, we investigate the behavior of THF, a typical battery solvent, on the surface of MoS₂, using ¹³C NMR. We have studied pure MoS₂ and MoS₂ intercalated with Li to compositions LiMoS₂ and Li₃MoS₂.

Materials

MoS₂ for catalytic purposes is commonly prepared on a support, typically $Al_2O_3^2$ For the present investigation, the possibility of THF interactions with support material made it desirable to study pure unsupported MoS₂. Since THF is not readily available with ¹³C enrichment, it was necessary to carry out this investigation with ¹³C at natural abundance. This, in turn, required MoS₂ samples of high surface area, in order that spectra of adsorbed monolayers could be recorded in reasonable times. After many unsuccessful attempts, it was found that high surface area MoS_2 could be consistently prepared from ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$ (ATTM). It was found essential to use freshly prepared ATTM. Initial chemical decomposition leads to MoS_3 , which was then reduced to MoS_2 .

Our detailed method of preparation was as follows: ATTM was prepared by bubbling gaseous H₂S (Matheson tech. grade) through an aqueous solution of $(NH_4)_2MoO_4$ (Equity Mines) made alkaline with NH₃.³ ATTM was decomposed to MoS₃ by addition of 5% formic acid to an H2S-saturated solution of ATTM and NH_3 ⁴ The MoS₃ was reduced to MoS₂ by heating in a 15% H₂/He mixture for 2 h at 250 °C. Our thermogravimetric studies show that MoS_2 is stable in H_2 up to 600 °C; lower temperatures were used in our preparations in order to obtain as large a surface area as possible.

MoS₂ samples prepared in this manner had S:Mo ratios, determined by thermogravimetric analysis, in the range 2.00-2.05. Surface areas (BET) ranged from 70 to 110 m^2/g and bulk densities from 1.9 to 2.1 g/cm³. X-ray powder diffraction of these samples showed typically four broad (several degrees) lines in the range $2\theta = 10-60^{\circ}$. Comparison with the powder pattern of well-crystallized 2H-MoS₂ indicates that the broad peaks from the high-area sample correspond to the (002), (100) + (101), (103), and (110) + (112) reflections of this polytope. Only the (002) reflection is free from overlap with other lines, and analysis of its width using the Scherrer formula suggests that a typical crystallite contains three layers of the MoS₂ structure.

Lithiated samples were prepared by reaction of MoS₂ with Li in liquid NH₃ under an atmosphere of Ar. Typically a calculated amount of Li foil (Foote) was dissolved in 30-50 mL of NH₃ at -78 °C, producing a deep blue solution. One to four grams of MoS_2 was then added, and within minutes the blue colour disappeared, as Li intercalated into the MoS₂. NH₃ was then removed by warming to room temperature under Ar, followed by vacuum treatment at 200-250 °C for 12 h, to remove any cointercalated NH₃. These samples had BET areas of $40-75 \text{ m}^2/\text{g}$ and bulk densities of 0.9-1.2 g/cm³. Li content was determined by ion chromatography. The LiMoS₂ sample had a Li:Mo ratio of 1.02 and the Li_3MoS_2 sample a ratio of 3.19. We were unable to obtain any clearly defined X-ray lines from the lithiated samples.



Figure 1. ¹³C CP/MAS spectra of THF on O-treated MoS₂: (A) Spectrum after adsorption at room temperature. (B-H) Spectra after successive 3-h heatings to 100, 150, 200, 250, 300, 350, and 400 °C, respectively. Heating to 500 °C produces no further spectral changes. Spectra recorded with (2.4×10^5) - (3.3×10^5) single-contact cross-polarizations. Contact time, 2 ms; recycle delay, 200 ms. Scale is in ppm with respect to TMS.

The investigation is difficult, due to the strong lines from the Be windows of the air-tight cell which must be used for the investigation of these materials. It appears, however, that the lithiated materials are less well crystallized than the parent MoS_2 . The data of Selwyn et. al.⁵ suggest that "Li₃MoS₂" is in fact a mixture of compounds.

Tetrahydrofuran was Fisher reagent grade. It was dried over 4A molecular sieves, followed by repurification over a lithium benzophenone ketyl solution, and stored under He until use.

Experimental Section

Samples of MoS₂ were placed in 5-mm NMR tubes and treated with H_2 at 250 °C on a vacuum line to remove adsorbed oxygen. Hydrogen was subsequently removed by pumping at the same temperature. TPD studies by Miremadi and Morrison⁶ on single-layer and multilayer MoS_2 show that H_2 does not intercalate under these conditions. For some samples, a known amount of O_2 was then chemisorbed at room temperature, to simulate a MoS_2 surface which has been exposed to air. Known amounts of THF were then adsorbed, using gas-volumetric measurement techniques. The samples were then sealed and ¹³C NMR spectra obtained by Hartmann-Hahn cross-polarization, with magic angle spinning, using a previously described⁷ spinner. A delayed decoupling sequence⁸ was used to identify nonprotonated carbons, and in some cases spectra were excited by 90° pulses, to examine small mobile molecules. The magnetic field used was 1.4 T, giving a ¹³C resonance frequency of 15.1 MHz.

Li_xMoS₂ samples were prepared as described above and transferred to the vacuum line under an inert gas atmosphere. NMR samples were prepared in the same way, without the initial H_2 reduction or O_2 chemisorption.

After recording of the initial spectra, the samples were heated to successively higher temperatures in an oven. After each heating

⁽²⁾ Furimsky, E. Catal. Rev.-Sci. Eng. 1980, 22, 371.
(3) Brauer, G., Ed. Handbook of Preparative Inorganic Chemistry; Academic Press Inc.: New York, 1963; Vol 1, p 1416.
(4) Auborn, J. J.; Barberio, Y. L.; Hanson, K. J.; Schleich, D. M.; Martin, M. J. J. Electrochem. Soc. 1987, 134, 580.

⁽⁵⁾ Selwyn, L. S.; McKinnon, W. R.; von Sacken, U.; Jones, C. A. Solid State Ionics 1987, 22, 337.

⁽⁶⁾ Miremadi, B.; Morrison, S. R., private communication.
(7) Gay, I. D. J. Magn. Reson. 1984, 58, 413.
(8) Opella, S. J.; Frey, M. H. J. Am. Chem. Soc. 1979, 101, 5854.

TABLE I: CP/MAS Results for THF on Reduced MoS,

temp, °C	resonances, ppm	assignments		
20-100	27, 69	unreacted THF		
150-200	13-16, 40, 190-200 (H) ^a	butanal		
	130-140	aromatic		
250-300	14, 25	CH ₃ , CH ₂		
	130	aromatic		
350	9, 16, 129			
400-500	129	aromatic		

 a (H) indicates direct-bonded H demonstrated by delayed decoupling.

TABLE II: CP/MAS Results for THF on Oxygen-Treated MoS₂

temp, °C	resonances, ppm	assignments		
20-100	26, 69	unreacted THF		
150-200	13-16, 42, 190-200 (H) ^a 29-31	butanal		
	126	aromatic		
	173-175	carboxylate		
250	13, 20, 39–42, 195 (H) ^a	butanal		
	20, 30	CH2		
	130	aromatic		
300-350	5	ethane?		
	16	CH3		
	24	CH,		
	129	aromatic		
400-500	130	aromatic		

"See footnote to Table I.

period of 3 h the samples were cooled to room temperature and the spectra remeasured.

Results

At room temperature, THF adsorbs on our MoS₂ samples to the extent of 5-6 μ mol/m² at a pressure of a few Torr. The CP/MAS spectrum of such a layer is shown in Figure 1A. As can be seen, the resonances correspond to those of liquid THF, which are at 68.6 and 26.7 ppm.⁹ If magic angle spinning is not used, the lines broaden to 300-400 Hz (20-27 ppm) but remain symmetrical in appearance. The initial spectra are similar on both reduced and oxygen-treated MoS₂ and on Li_xMoS₂. The proton T_1 for the adsorbed layer is approximately 50 ms, and the cross-polarization time constant is about 200 μ s.

The two unshifted lines observed at room temperature indicate that THF has adsorbed intact. There must be considerable motion in the adsorbed layer, leading to partial averaging of the chemical shift anisotropy, otherwise a nonspinning spectrum should show powder patterns up to 80 ppm wide.¹⁰ Since cross-polarization is reasonably rapid, the average C-H dipolar coupling must be substantial, and the molecules cannot be rotating isotropically. A reasonable adsorption model would be complexation of THF to surface Mo via the O. Rotation of the molecule about the Mo-O bond, together with some reorientation of this bond axis, would account for the NMR results.

The adsorbed THF layers appear to be stable indefinitely at room temperature. Upon heating to higher temperatures, spectral changes are observed, as shown, for example, in Figure 1B-H. On all surfaces the original THF lines disappear, and new lines arise in regions characteristic of aliphatic, aromatic, and carbonyl carbons. A list of lines, observed by CP/MAS spectroscopy, together with assignments where possible, is given in Tables I-IV.

In addition to these lines, ¹³C spectroscopy with 90° pulses reveals the presence of small mobile molecules at the higher temperatures. Butane appears near 250 °C, followed by propane, ethane, and ethylene as the temperature is raised. Methane and carbon dioxide are the only gases present after heating to 500 °C.

TABLE III:	CP/	/MAS	Results	for	THF	on	LiMo	S
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ter	np, °C	resonances, ppm	assignments	-	
20-200 250-300 350-400		26, 70 12, 19, 40, 184 (H) ^a 12, 20, 31	unreacted THF butanal isopentane?		
		130	aromatic		

"See footnote to Table I.

FABLE IV:	CP/MAS	Results for	THF on	Li ₃ MoS ₂
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temp, °C	resonances, ppm	assignments
20-150	26, 69	unreacted THF
150-200	13, 20, 35, 61	butoxide
	26	CH,
250-300	13, 21	CH_{3}, CH_{2}
	32, 39	branched aliphatic
	51	OCH ₃
300-350	gradual disappearance of all CP/MAS peaks	÷

The presence of these gases was confirmed by GC/MS experiments.

A control experiment was performed in order to verify that the observed reactions were surface reactions and not simply thermal decomposition of THF. On all samples, the THF peaks have completely disappeared after heating at 250 °C. We therefore heated a sample of pure THF at 250 °C in a stainless steel container for 3 h. After cooling, the gas phase was analyzed by GC/MS and the liquid phase by high-resolution proton NMR. In neither case was any substance other than THF detected. The NMR analysis of the liquid would have detected 0.1% of reaction products. We thus conclude that the initial reaction of THF is indeed dependent on the presence of the MoS₂ surface. This agrees with the results of Klute and Walters,¹¹ who found that homogeneous decomposition of THF takes place above 500 °C.

It should be noted that the assignments in the tables are not completely unambiguous. Thus, the peak near 130 ppm found on all samples (except Li_3MoS_2) at high temperatures has been assigned as aromatics. The chemical shift could equally well correspond to olefinic carbon. However, this peak persists to the highest temperatures, where no bound aliphatic carbon is seen. Delayed decoupling shows it to contain about 50% protonated carbon. In addition, we have tried unsuccessfully to remove this material from the surface by solvent extraction with acetone and carbon tetrachloride. These facts taken together make it most likely that this is a high molecular weight condensed aromatic residue.

There is surprisingly little difference in results among the first three surfaces studied. The most striking difference being the higher temperature required to produce reaction on LiMoS₂. On reduced and oxidized MoS₂ and on LiMoS₂, the initial reaction product appears to be butanal. We make this assignment on the basis of the simultaneous appearance and subsequent disappearance of peaks at 13-16, 39-41, and 190-200 ppm. The last being shown by delayed decoupling to have a bonded H. Butanal in the liquid phase has shifts¹² of 13.3, 15.7, 45.7 and 201.6 ppm. While the agreement is not exact, an aldehyde is clearly indicated, and, allowing for small shifts on adsorption, butanal seems the most reasonable. The general trend of subsequent thermal evolution leads to the decomposition of the adsorbed layer, producing eventually gaseous CO₂ and small hydrocarbons, together with condensed aromatic residues on the surface. In the case of the oxidized MoS₂ surface, an additional carboxylate intermediate is observed. This must result from the oxidation of the initial aldehyde product by the chemisorbed O.

The reactivity pattern was quite different with Li_3MoS_2 . On this surface the initial aldehyde product was not seen, rather a butoxide is observed. High-temperature treatment eventually produces small gaseous hydrocarbons, but no CO_2 or surface

⁽⁹⁾ Standard Carbon-13 NMR Spectra; Sadtler Research Laboratories, Inc.: Philadelphia, 1976.

⁽¹⁰⁾ Facelli, J. C.; Orendt, A. M.; Beeler, A. J.; Solum, M. S.; Depke, G.; Malsch, K. D.; Downing, J. W.; Murthy, P. S.; Grant, D. M.; Michl, J. J. Am. Chem. Soc. 1985, 107, 6749.

 ⁽¹¹⁾ Klute, C. H.; Walters, W. D. J. Am. Chem. Soc. 1946, 68, 506.
 (12) Stothers, J. B. Carbon-13 NMR Spectroscopy; Academic Press: New York, 1972.

aromatics. This appears reasonable, in view of the much higher reducing ability of this sample. Probably the oxygen from THF ends as lithium oxide or carbonate. The nonappearance of surface aromatics in this case suggests that these arise from thermal evolution of O-containing species, possibly the initial aldehyde.

Conclusion

While we have exhibited a range of hitherto unexplored surface chemistry, we have not illuminated the question of electrolyte decomposition in Li-MoS₂ batteries. Our results show clearly that THF is stable for long periods of time in contact with MoS_2 or lithiated MoS₂ at room temperature. No reactivity was observed at temperatures below 150 °C, which is above the range of operation of lithium/organic electrolyte battery systems. The observed electrolyte decomposition in batteries must therefore have an explicitly electrochemical origin, or must involve reactions with some other battery component.

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Registry No. THF, 109-99-9; MoS₂, 1317-33-5; LiMoS₂, 12201-18-2; Li₃MoS₂, 136676-60-3.

Surface-Enhanced Infrared Absorption of *p*-Nitrobenzoic Acid Deposited on Silver Island Films: Contributions of Electromagnetic and Chemical Mechanisms

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We have studied the infrared transmission spectra of thin organic films of p-nitrobenzoic acid deposited on silver island films evaporated on CaF₂. The absorption of the molecule is enhanced remarkably by the presence of silver island films. When mass thickness of the silver film is very small, the enhancement is restricted only to the molecule adsorbed directly onto the silver surface. As the mass thickness increases, the absorption intensity of the chemisorbed molecule increases and, in addition, the absorption of the molecules that were condensed over the chemisorbed molecule becomes to be enhanced. The largest enhancement factor is 500-600 for the chemisorbed molecule and is 20-30 for the overlayer. It has been suggested that the enhancement of electromagnetic field and the increase in vibrational polarizabilities of the molecule caused by a chemical interaction with the metal surface contribute independently to the absorption enhancement. Orientation of the chemisorbed molecule provides further additional small enhancement. The observed quite large enhancement is explained by a product of these three contributions.

Introduction

Optical properties of molecules are altered dramatically when they are adsorbed on or near some rough metal surfaces. Surface-enhanced Raman scattering (SERS) is the most prominent example.¹⁻⁴ Recently, SERS was observed for near-infrared (near-IR) excitation (1.06 μ m from a Nd:YAG laser) as strong as for the SERS for visible excitations.⁵⁻⁷ Similar surface-enhanced phenomenon is observed also in the infrared (IR) region. Hartstein et al.⁸ found that IR absorption of organic thin films is enhanced remarkably by the presence of very thin overlayer or underlayer of silver or gold with a use of attenuated total reflection (ATR) technique. Since the discovery, the surfaceenhanced IR absorption (SEIRA) has been investigated by several groups.⁹⁻²⁰ The SEIRA was observed also in the external reflection and transmission geometries.13,17

The SEIRA spectroscopy in the ATR geometry was successfully applied to in situ characterization of molecules adsorbed at electrode/electrolyte interfaces¹¹ and of thin organic layers.^{10,12,13} Recently, its potential for trace organic analysis has been explored.¹⁷ Nanogram quantities of molecules were detected in the transmission measurements by spotting sample solution onto the silver-coated IR transparent substrates. If an FT-IR microspectrometer is available, the detection limit can be reduced to subpicogram order.^{17,21} However, the mechanism of SEIRA is not fully understood.

Island structure of the very thin metal film plays an important role in SEIRA.⁸ It has been proposed that the enhancement is

due to a strong electromagnetic (EM) field amplified through the excitation of collective electron resonance (localized plasma os-

- (1) Chang, R. K., Furtak, T. E., Eds. Surface Enhanced Raman Scattering; Plenum Press: New York, 1982
 - (2) Metiu, H. Prog. Surface Sci. 1984, 17, 153
 - (3) Moskovits, M. Rev. Mod. Phys. 1985, 57, 783.
- (4) Otto, A. In Light Scattering in Solids; Cardona, M., Guntherodt, G.,
- Eds.; Springer: Berlin, 1983; Vol. IV, Chapter 6.
- (5) Crookell, A.; Fleischmann, M.; Hanniet, M.; Hendra, P. J. Chem. Phys. Lett. 1988, 149, 123.
 - (6) Chase, D. B.; Parkinson, B. A. Appl. Spectrosc. 1988, 42, 1186.
- (7) Angel, S. M.; Katz, L. F.; Archibald, D. D.; Honigs, D. E. Appl. Spectrosc. 1989, 43, 367.
- (8) Hartstein, A.; Kirtley, J. R.; Tsang, T. C. Phys. Rev. Lett. 1980, 45, 201
- (9) Hatta, A.; Suzuki, Y.; Suëtaka, W. Appl. Phys. A 1984, 35, 135. (10) Sigarev, A. A.; Yakovlev, V. A. Opt. Spectrosc. (Engl. Transl.) 1984, 56, 336.
- (11) Hatta, A.; Chiba, Y.; Suëtaka, W. Appl. Surface Sci. 1986, 25, 327. (12) Nakao, Y.; Yamada, H. Surface Sci. 1986, 176, 578.
 (13) Kamata, T.; Kato, A.; Umemura, J.; Takenaka, T. Langmuir 1987,
- 3, 1150.
- (14) Osawa, M.; Kuramitsu, M.; Hatta, A.; Sučtaka, W.; Seki, H. Surface Sci. 1986, 175, L787.
- (15) Suzuki, Y.; Osawa, M.; Hatta, A.; Suëtaka, W. Appl. Surface Sci. 1988. 33/34, 875.
- (16) Hatta, A.; Suzuki, N.; Suzuki, Y.; Suëtaka, W. Appl. Surface Sci. 1989, 37, 299.
- (17) Nishikawa, Y.; Fujiwara, K.; Shima, T. Appl. Spectrosc. 1990, 44, 691
- (18) Wadayama, T.; Sakurai, T.; Ichikawa, S.; Suētaka, W. Surface Sci. 1988, 198, L359.
- (19) Badilescu, S.; Ashrit, P. V.; Truong, V.-V. Appl. Phys. Lett. 1988, 52. 1551
- (20) Badilescu, S.; Ashrit, P. V.; Truong, V.-V.; Badilescu, I. I. Appl. Spectrosc. 1989, 43, 549.

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