

Figure 15. Effect of atomic oxygen upon the B(1s) and N(1s) XPS spectra for boron-nitrogen adlayers on Ru(0001): (a) after dosing NH_3 (first) and B_2H_6 (second) at 90 K and subsequent annealing to 1000 K ($\theta_{\text{B}} = 0.33$ ML and $\theta_{\text{N}} = 0.18$ ML); (b) after dosing 0.4 ML of O at 300 K; (c) and (d) after annealing the surface that gave spectra b to 800 and 1000 K ($\theta_{\text{B}} = 0.33$ ML, $\theta_{\text{N}} = 0.08$ ML, and $\theta_{\text{O}} = 0.4$ ML).

oxygen reduced the stability of the boron-nitrogen adlayer by weakening the B-N bonds. Annealing of the O/B/N/Ru(0001) surface from 300 K to 800 and 1000 K induced an appreciable loss of nitrogen atoms (see Figure 15), a phenomenon that was not observed for the B/N/Ru(0001) surface. The B(1s) peak position seen in Figure 15 for spectrum d is very close to those displayed in Figures 13 and 14 for the boron-oxygen adlayers.

The results of this section indicate quite clearly that diborane will react preferentially with oxygen impurities during the preparation of boron-nitride films from $\text{B}_2\text{H}_6 + \text{NH}_3$, producing coatings with a low level of thermal stability.

IV. Conclusions

- (1) At a temperature of 500 K, diborane dissociates completely

on Ru(0001), producing boron adatoms and H_2 gas. The saturation coverage of B on Ru(0001) is ~ 1.1 ML. At this coverage, part of the B adlayer can be removed from the surface by heating to 1250 K, with a large fraction of the B atoms still adsorbed at 1450 K.

- (2) B_2H_6 thermal desorption spectra acquired after adsorption of diborane on Ru(0001) at 90 K showed a sharp peak at 150 K (multilayer desorption) and a broad feature between 250 and 400 K (monolayer desorption). Evolution of H_2 was observed from 250 to 400 K. Above 400 K, only atomic boron was left on the surface. The maximum coverage of boron atoms produced during these experiments was 0.42 ML.

- (3) On the clean, well-ordered Ru(0001) surface, ammonia adsorbed molecularly. Saturated Ru(0001) surfaces showed NH_3 features at ~ 110 (multilayer desorption), 135 (second monolayer), 190, and 285 K (first monolayer). Under ultrahigh vacuum conditions the amount of ammonia that dissociated on B/Ru(0001) surfaces was negligible. For $\theta_{\text{B}} < 0.5$ ML, the B- NH_3 interaction enhanced the adsorption energy of ammonia on Ru(0001). A new NH_3 desorption state at ~ 350 K was observed in the presence of boron adatoms.

- (4) Boron-nitrogen adlayers were formed: (a) by exposing B/Ru(0001) surfaces at 600 K to high pressures (5-10 Torr) of NH_3 ; and (b) after coadsorption of NH_3 (dosed first) and B_2H_6 (dosed second) at 90 K, and subsequent annealing to temperatures above 600 K. The boron-nitrogen overlayers were rich in boron and decomposed at temperatures above 1100 K.

- (5) On O/Ru(0001) surfaces, diborane was adsorbed dissociatively forming B-O bonds. Adsorbed atomic oxygen reduced the stability of the boron-nitrogen adlayers on Ru(0001).

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Registry No. B_2H_6 , 19287-45-7; Ru, 7440-18-8; NH_3 , 7664-41-7; O, 17778-80-2; BN, 10043-11-5.

Molecular Precursors to Boron Nitride Thin Films. 2. Coadsorption and Reaction of Hydrazine and Diborane on Ru(0001)

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The adsorption of hydrazine (N_2H_4) on clean Ru(0001) and its coadsorption and reaction with diborane (B_2H_6) have been studied by means of thermal desorption mass spectroscopy, X-ray photoelectron spectroscopy, Auger electron spectroscopy, and Fourier-transform infrared reflectance absorption spectroscopy. On clean Ru(0001), desorption of N_2H_4 was observed at temperatures of 185 (multilayer state) and 280 K (monolayer state, desorption energy ~ 17 kcal/mol). Adsorbed hydrazine decomposed extensively into NH_3 , N_2 , N, and H. TDS spectra from N/Ru(0001) surfaces showed N_2 evolution in a sharp peak at ~ 510 K and in a broad feature between 600 and 800 K. Boron-nitrogen adlayers with stoichiometry close to 1:1 were formed: (a) by simultaneous dosing of B_2H_6 and N_2H_4 at 450 K, and (b) after coadsorption of B_2H_6 and N_2H_4 at 90 K and subsequent heating to 450 K. These adlayers decomposed at temperatures above 1100 K.

I. Introduction

Stoichiometric boron nitride (BN) is distinguished by its remarkable hardness and its ability to withstand high temperatures. In addition, this material shows a low density and a high chemical inertness. These physical and chemical properties make boron nitride useful for thermal insulation, as a die wash material, and as a lubrication and pressure-transmission medium.¹⁻³ Considerable effort has been focused on developing routes to synthesize

BN in thin film forms.¹⁻⁴ In the preceding article in this journal, we used diborane (B_2H_6) and ammonia (NH_3) as molecular precursors for the synthesis of BN films on Ru(0001). Due to the unusual chemical stability of ammonia, a very low reactivity

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between B_2H_6 and NH_3 was observed under ultrahigh vacuum (UHV) conditions. The boron–nitrogen overlayers were rich in boron (B/N atomic ratio ~ 1.8) and decomposed at temperatures above 1100 K.⁴ In the present work we replace NH_3 with the more reactive species, hydrazine (N_2H_4). The interaction between N_2H_4 and B_2H_6 on Ru(0001) is investigated using thermal desorption mass spectroscopy (TDS), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and Fourier-transform infrared reflectance absorption spectroscopy (FT-IRAS).

For a detailed discussion of the surface chemistry of B_2H_6 on Ru(0001), we refer the reader to the preceding paper in this journal. To the best of our knowledge, no study has appeared examining the adsorption of hydrazine on Ru(0001). Previous works for adsorption of the molecule on Fe(111),⁵ Ni(100),⁶ Rh(100),^{7a} polycrystalline Rh,^{7b} and polycrystalline Al⁸ indicate extensive decomposition into nitrogen, hydrogen, and ammonia.

This article begins with a discussion of studies on the adsorption and decomposition of hydrazine on Ru(0001). Next, the results of the coadsorption of B_2H_6 and N_2H_4 , and the synthesis of B_mN_n overlayers are presented. Finally, we show studies dealing with the interaction of O_2 and B_mN_n films supported on Ru(0001).

II. Experimental Section

The experimental set up used in this study is identical to that described in the preceding paper in this journal. All XPS spectra were recorded with Al K α radiation. The variations in the binding energies of the B(1s) and N(1s) regions were determined by referencing against the Ru(3d_{5/2}) and Ru(3p_{1/2}) peaks, which were set at binding energies of 280 and 483 eV, respectively. The Ru(0001) crystal was cleaned following procedures reported in the literature.^{4,9,10} C, N, and B were removed from the surface by heating in 5×10^{-8} Torr of O_2 at 1100 K for 5 min, followed by flashing to 1650 K. This procedure was repeated until the surface was determined to have <1% impurities as indicated by AES and XPS. Prior to each use, the B_2H_6 reagent, diluted in Ar for storage, was condensed and the Ar pumped away. Anhydrous N_2H_4 from Sigma Chemical was used after purification by cooling to ~ 260 K and evacuation of any possible decomposition products (hydrogen, nitrogen, and ammonia).

In this work, adsorbate coverages are reported with respect to the number of Ru(0001) surface atoms (1.57×10^{15} atoms/cm²). One adatom per substrate surface atom corresponds to $\theta = 1.0$ ML (monolayer). The N coverages were determined by measuring the N(1s)/Ru(3d) XPS intensity ratio. This ratio was calibrated to absolute coverage units by using the corresponding value measured in our instrument for a saturated layer of chemisorbed ammonia on Ru(0001) ($\theta_{NH_3} = 0.25$ ML¹¹). The amount of boron on the surface was measured by using the B(1s)/Ru(3d) XPS intensity ratio, which was scaled to absolute coverage following the method described in ref 4.

III. Results and Discussion

III.1 Hydrazine Adsorption on Clean Ru(0001). A. Adsorption at 90 K. Figure 1 shows thermal desorption spectra acquired after a saturation exposure of hydrazine to Ru(0001) at 90 K. These results indicated that adsorbed hydrazine decomposes into ammonia, hydrogen, and nitrogen. The only nitrogen–hydrogen species desorbing from the surface in the experiments were NH_3 and N_2H_4 . Signals observed for other nitrogen–hydrogen species were part of the cracking pattern of N_2H_4 and NH_3 in the mass spectrometer.

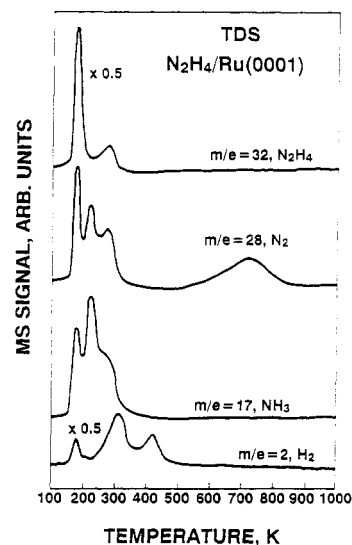


Figure 1. Thermal desorption spectra acquired after dosing multilayers of hydrazine to clean Ru(0001) at a temperature of ~ 90 K. Heating rate 7 K/s.

Two peaks appear in the N_2H_4 -TDS spectra of hydrazine on Ru(0001). The state at ~ 185 K can be attributed to the desorption of the N_2H_4 multilayer, since it grew continuously with exposure without saturation. In previous studies,⁷ a temperature of 190 K was reported for N_2H_4 multilayer desorption from Rh(100). The state at ~ 280 K can be assigned to monolayer desorption. Assuming first-order desorption and a typical preexponential factor of 10^{13} s⁻¹, a standard Redhead analysis¹² yields a desorption activation energy of 16.6 kcal/mol for chemisorbed hydrazine on Ru(0001).

In Figure 1 the thermal desorption spectrum for H_2 evolution shows peaks at approximately 185, 320, and 425 K. No desorption of H_2 was found at temperatures higher than 450 K. In our experiments, no saturation was observed for the H_2 -TDS peak at 185 K. This feature appears simultaneously with N_2H_4 desorption and is a consequence of the cracking of hydrazine in the mass spectrometer. The H_2 -desorption peaks between 200 and 450 K are a consequence of the decomposition of chemisorbed hydrazine. The feature at ~ 320 K is probably rate-limited by the associative desorption of adsorbed hydrogen atoms ($2H_a \rightarrow H_2$) rather than by N–H bond cleavage, since this peak is very similar in temperature and shape to that for H_2 desorption from hydrogen adatoms on Ru(0001).^{13,14} On the other hand, the feature at ~ 425 K is rate-limited by the scission of N–H bonds in a NH_2 intermediate.

The range of temperatures observed in Figure 1 for NH_3 evolution is very similar to that found for NH_3 /Ru(0001),^{4,11} but the line shape of the TDS spectrum is different in each case. The desorption spectrum of ammonia on clean Ru(0001) does not show a sharp peak at 225 K.^{4,11} In Figure 1, the NH_3 feature at 225 K is accompanied by simultaneous desorption of N_2 into gas phase. On Ru(0001), N adatoms recombine into N_2 at temperatures above 480 K (see below). On the other hand, adsorbed molecular nitrogen desorbs below 130 K.¹⁵ Thus the data of Figure 1 are consistent with a reaction pathway in which a nitrogen–hydrogen adspecies decomposes at 225 K producing NH_3 , N_2 (which desorbs), and hydrogen adatoms.

The N_2 -TDS spectrum of hydrazine on Ru(0001) displays peaks at 185, 225, and 280 K and a broad feature between 500

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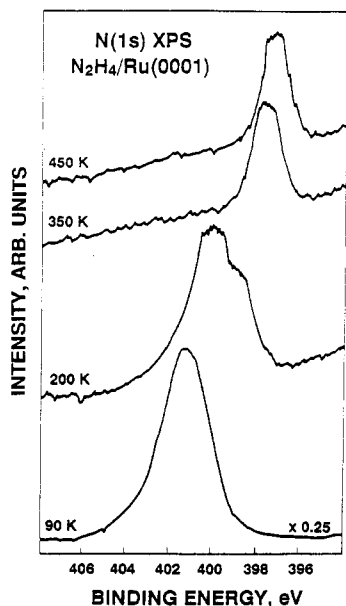


Figure 2. N(1s) XPS spectra taken after dosing ~ 5 ML of hydrazine to Ru(0001) at 90 K. Before acquiring the spectra, the surface was heated to the temperatures indicated in the left side of the figure. Annealing from 90 to 200 K induced desorption of the N₂H₄ multilayer (see Figure 1). From 200 to 350 K, N₂ and NH₃ evolved from the surface (see Figure 1). Above 450 K, only atomic N was on the surface.

and 800 K. The peak at 185 K corresponds to the cracking of N₂H₄ multilayers in the mass spectrometer, whereas the peaks at 225 and 280 K are mainly a result of decomposition reactions that yield molecular nitrogen on the Ru(0001) surface. At 450 K, the only species present on the surface is atomic nitrogen (see below). The N₂-TDS feature between 500 and 800 K is a consequence of the recombination of nitrogen adatoms.

Figure 2 shows a N(1s) XPS spectrum acquired after adsorbing ~ 5 ML of hydrazine on Ru(0001) at 90 K. The peak position is centered at ~ 401.4 eV. This value agrees well with those reported for N₂H₄ multilayers on Fe(111)⁵ and Rh(100).⁷ Flashing the crystal to 200 K induced desorption of the hydrazine multilayers (see Figure 1), leaving only chemisorbed species ($\theta_N \approx 0.55$ ML). The corresponding N(1s) spectrum is characterized by the presence of two overlapping peaks. The peak maximum at higher binding energy is located at ~ 400.1 eV, very close to the value observed in our instrument for ammonia chemisorbed on Ru(0001)⁴ and to values reported in the literature for hydrazine chemisorbed on Fe(111),⁵ Rh(100),⁷ and polycrystalline Al.⁸ On the other hand, the peak at lower binding energy is centered at ~ 399 eV. The identity of the species responsible for this feature is unknown. It may be argued that the overlapping peaks are a result of different chemical environments for the nitrogens of hydrazine. For an "end on" bonded hydrazine molecule, two N(1s) peaks can be expected, since the outer nitrogen atom should have a negative excess charge when compared to the nitrogen bonded to the metal surface.^{5,9} In the XPS spectrum of C₅H₅Mn(CO)₂N₂H₄ this doublet was not resolved, but a broad feature with a half-width of ~ 3.8 eV was observed.¹⁸ The half-width of the spectrum at 200 K in Figure 2 is only 3 eV. This, together with the fact that the two overlapping peaks have different intensities, indicates that an "end on" bonded hydrazine species is not responsible for the 200 K spectrum. A more plausible explanation is that a fraction of the adsorbed N₂H₄ molecules decomposes at temperatures below 200 K.

Further heating to 350 K induced a large decrease in the N(1s) signal as a consequence of N₂ and NH₃ desorption (see Figure 1). The spectrum is now centered at 397.7 eV. This binding energy is similar to values seen for NH (imide) species on metal surfaces.^{5,8} Finally, heating of the surface to 450 K produced a N(1s) peak situated at 397.2 eV that can be attributed to nitrogen

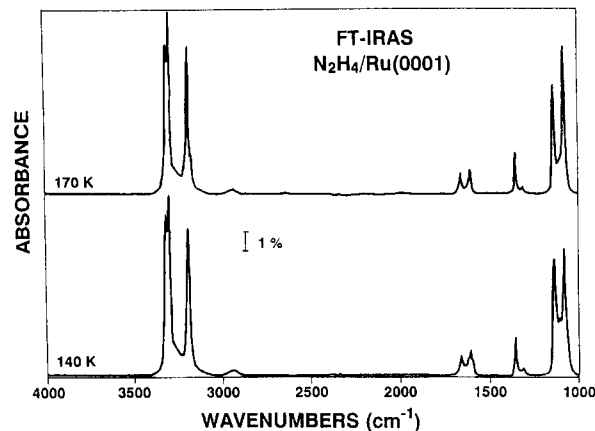
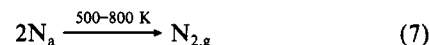
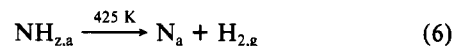
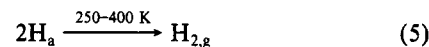
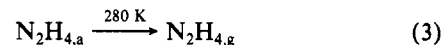
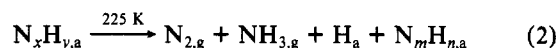
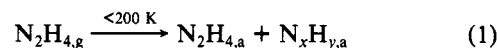


Figure 3. FT-IRAS spectra for a 4–5 layer N₂H₄ film. Hydrazine was dosed at 140 K to the Ru(0001) surface. The spectra were acquired after annealing the surface to the temperatures indicated in the left side of the figure.

adatoms ($\theta_N \approx 0.22$ ML). N(1s) binding energies between 397.0 and 397.4 eV have been reported for nitrogen atoms adsorbed on metal surfaces.^{5,8,17} No N(1s) signal was observed after annealing the crystal to 850 K. The N adatoms recombine and desorb as N₂ at temperatures between 500 and 800 K (see Figure 1).

The TDS and XPS results are consistent with the following reaction scheme for hydrazine on Ru(0001):



The exact stoichiometry of the N_xH_y, N_mH_n, and NH_z species is unknown at the present time. During the TDS experiments, neither NH₂ nor NH were detected with the mass spectrometer as desorption products from the surface. In the literature N₂H₃, N₂H₂, NH₂, and NH have been proposed as intermediates in the dissociation of hydrazine on metals.^{5,7,8,16}

Figure 3 gives FT-IRAS results for a saturation coverage of hydrazine on Ru(0001). The spectra correspond to a condensed film that is 4–5 layers thick. Above 180 K (desorption temperature of N₂H₄ multilayers), no feature that could be attributed to an adsorbed nitrogen–hydrogen species was observed. This is a consequence of the low cross-section of the vibrational modes associated with adsorbed N_xH_y species. The spectra of Figure 3 are in good agreement with infrared spectra for condensed hydrazine.¹⁹ The bands between 3150 and 3350 cm^{−1} have been assigned to stretching modes of the HNH groups.^{20a} The peak at 1080 cm^{−1} corresponds to the N–N stretch.^{20a} The features at 1305 and 1335 cm^{−1} are the product of twisting modes of the molecule, whereas those at 1605 and 1660 cm^{−1} are a consequence of scissor modes.²⁰

The data presented above indicate that hydrazine is extremely reactive on Ru(0001), decomposing into NH₃, N₂, N, and H. The large reactivity of N₂H₄ is a consequence of combining two mo-

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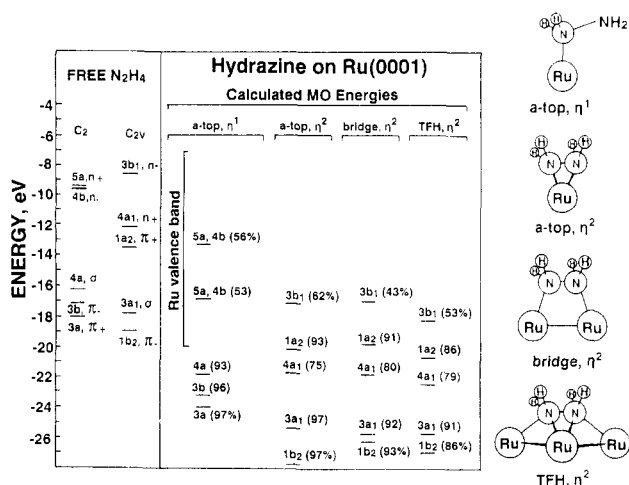


Figure 4. Calculated energies with INDO/1 for the occupied molecular orbitals of free and adsorbed hydrazine (from ref 9). The molecule was adsorbed in the configurations displayed in the right side of the figure. TFH denotes adsorption on adjacent 3-fold hollow sites. The local symmetry of adsorbed N₂H₄ was C₂ (a-top- η^1) or C_{2v} (η^2 conformations). The MO energies are reported with respect to the vacuum level. The numbers in parentheses represent the percentage of N₂H₄ character in each orbital.

molecular properties: a weak N-N bond (H₂N-NH₂ → 2NH₂, $\Delta E \approx 65$ kcal/mol²¹) and the presence of two N lone pairs that facilitate bonding interactions with the metal surface. Recently, we have investigated the interaction between N₂H₄ and Ru(0001) at a molecular orbital level using the INDO/1 method.⁹ Hydrazine was adsorbed in the molecular conformations displayed in Figure 4. A bidentate species adsorbed on adjacent 3-fold hollow sites (TFH, η^2) showed the strongest bonding interactions with the Ru surface.⁹ In its ground state in the gas phase, the N₂H₄ molecule has C₂ symmetry.^{21b} The energy barrier between this conformation and a geometry with C_{2v} symmetry (~ 10 kcal/mol^{21b}) is easily overcome by the formation of Ru-N bonds.⁹

In all the cases examined,⁹ the chemisorption bond was mainly a consequence of interactions between the N lone pairs and the Ru (5p,4d) orbitals. The participation of the virtual orbitals of N₂H₄ in the adsorption bond was insignificant. This type of bonding led to a partial positive charge (0.5–0.7e) on the ad-molecule.⁹ Figure 4 summarizes the effects of chemisorption upon the molecular orbitals of N₂H₄.⁹ A picture of these orbitals is presented in ref 22. The main orbital characters are denoted by letters n, σ , and π which mean n(N), σ (N-H) and π (NH₂) orbitals, respectively. From Figure 4, it is clear that similar UPS spectra can be expected for all the η^2 forms of coordination and that these will be different from the UPS spectrum of a η^1 species. For η^2 forms of coordination, INDO/1 predicts a relative downward shift of the N lone pairs (3b₁ and 4a₁ orbitals) with respect to the 1a₂, 3a₁, and 1b₂ orbitals. This shift is a product of a strong overlap between the N lone pairs and the Ru orbitals. Adsorption in an a-top- η^1 geometry causes rehybridization of the N lone pairs (5a + 4b mixing), and among the resulting MO's only the one localized on the metal-bound N is shifted downward with respect to the N-N and NH₂ orbitals.

B. Adsorption at 450 K. The adsorption of hydrazine was also investigated at a surface temperature of 450 K. At this high temperature, the N₂H₄ molecule completely dissociates on Ru(0001) producing N adatoms and H₂ evolution. Figure 5 displays N(1s) XPS spectra for atomic nitrogen on Ru(0001). In all cases the peak position is close to 397.3 eV.

TDS spectra of N₂ ($m/e = 28$) from N/Ru(0001) are shown in Figure 6 as a function of N coverage. Identical line shapes

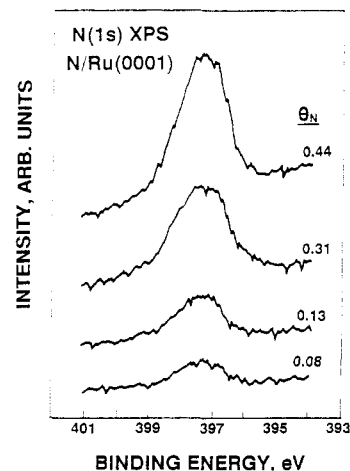


Figure 5. Effect of coverage upon the N(1s) XPS spectrum of atomic nitrogen on Ru(0001). The N adlayers were formed by dosing N₂H₄ to the surface at 450 K.

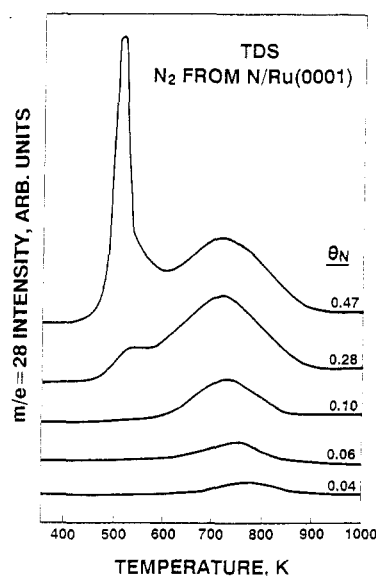


Figure 6. Representative thermal desorption spectra showing the evolution of N₂ from N/Ru(0001) surfaces. The N atoms were deposited by dosing N₂H₄ to Ru(0001) at 450 K. Heating rate 7 K/s.

were observed for the mass 14 spectra, with mass 28/mass 14 intensity ratios equal to the value expected for the cracking pattern of N₂. The spectra in Figure 6 are a product of the associative desorption of nitrogen atoms: 2N_a → N_{2,g}. On Ru(0001), adsorbed molecular nitrogen desorbs at temperatures below 130 K.¹⁵ At $\theta_N < 0.25$ ML, only a broad feature appears in the spectra for N₂ evolution. The center of this feature shifts from 770 to 715 K, consistent with a second-order atomic recombination mechanism. For $\theta_N > 0.25$ ML, a sharp desorption peak appears at temperatures between 500 and 550 K. Above 850 K, the AES and XPS spectra showed that no nitrogen was on the surface.

Following Redhead's expression for second order desorption¹² with a plot of $\ln(\theta_N T_p^2)$ versus $1/T_p$ for N₂-TDS data at $\theta_N < 0.25$ ML, a desorption energy of ~ 40.5 kcal/mol is deduced. The assumption of first-order desorption kinetics with a preexponential factor of 10^{13} s⁻¹¹² was also applied to the N₂-TDS data. Based on the variation of T_p with coverage, the first-order desorption energy is $E = (47 - 14\theta_N)$ kcal/mol for $0 < \theta_N < 0.25$ ML. Thus, the estimates of second-order and first-order desorption kinetics are similar, and a lower limit of 40 kcal/mol can be set for the desorption energy at small nitrogen coverages. The N₂-TDS peak at 510 K has a first-order desorption energy of 30.9 kcal/mol.

In Figure 6, N₂ evolution is seen between 480 and 850 K. N₂-desorption temperatures between 400 and 750 K have been previously observed for nitrogen adatoms generated by nitric oxide decomposition (NO_g → N_a + O_a) on Ru(0001).²³ It seems that

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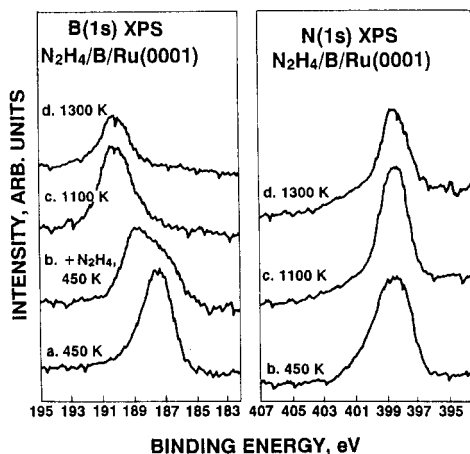


Figure 7. B(1s) and N(1s) XPS spectra for boron-nitrogen adlayers on Ru(0001) formed by reaction between atomic boron and N_2H_4 : (a) 0.53 ML of atomic boron on Ru(0001) after annealing to 450 K; (b) after exposure of the surface to 60 langmuir of N_2H_4 at 450 K; (c) and (d) after annealing the surface that gave spectra b to 1100 and 1300 K.

coadsorption with oxygen has only a moderate influence in the surface chemistry of nitrogen on Ru(0001). Although the line shape of our N_2 -TDS spectra is somewhat different from that of spectra reported in ref 23, in all cases there is a sharp desorption peak around 500 K.

III.2 Coadsorption of Hydrazine and Diborane on Ru(0001). The main objective of our work is to investigate the coadsorption of B_2H_6 and N_2H_4 as molecular precursors in the synthesis of boron nitride films. Our previous work examining the coadsorption of ammonia and diborane showed films with an excess in boron (B/N atomic ratio ~ 1.8) due to the low reactivity of NH_3 .⁴ Under ultrahigh vacuum conditions, the decomposition of ammonia on clean and boron covered Ru(0001) surfaces was negligible.⁴ Hydrazine shows a much larger reactivity than ammonia, and this facilitates the synthesis of films with B:N stoichiometries close to 1:1.

A. Adsorption of Hydrazine on B/Ru(0001) Surfaces. The effect of atomic boron on the decomposition of hydrazine on Ru(0001) was investigated at a temperature of 450 K. The boron precovered surfaces ($0.1 < \theta_B < 0.9$ ML) were generated by dissociation of diborane at 500 K.⁴ Nitrogen coverages between 0.5 and 1 ML were easily produced by using a hydrazine exposure of 90 langmuir. For $\theta_B < 0.5$ ML, overlayers with N/B atomic ratios greater than 1 were observed at 450 K. However, no film with a N/B ratio larger than 1 was seen upon heating to 1100 K.

Figure 7 shows typical XPS results obtained after exposing a surface with 0.53 ML of B to 60 langmuir of hydrazine. Initially, the B(1s) peak for atomic boron was centered at 187.5 eV. Reaction with nitrogen produced a significant broadening in the B(1s) spectrum (curve b). Upon heating to 1100 K, the adlayer showed a composition of 0.48 ML of B and 0.43 ML of N. At this temperature, the binding energies observed for the boron-nitrogen adlayer (B(1s), ~ 190.0 eV; N(1s), ~ 398.5 eV) are very different from the corresponding values for atomic boron and nitrogen on Ru(0001). Such large differences suggest that there are strong bonds between boron and nitrogen atoms. Indeed, the measured binding energies for the boron-nitrogen overlayer are within 0.6 eV of those reported for boron nitride.²⁴ Additional evidence that supports the hypothesis of bonding between the boron and nitrogen atoms comes from the fact that a very large amount of nitrogen was still present on the surface at 1100 K. Atomic nitrogen desorbs from clean Ru(0001) at temperatures below 850

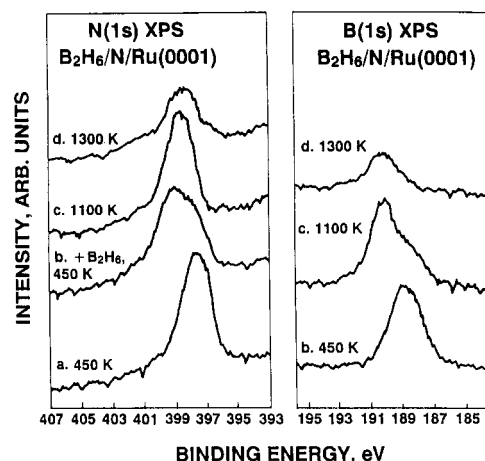


Figure 8. N(1s) and B(1s) XPS spectra for boron-nitrogen adlayers on Ru(0001) formed by reaction between diborane and atomic nitrogen: (a) 0.4 ML of atomic nitrogen after annealing to 450 K; (b) after exposure of the surface to 20 langmuir of B_2H_6 at 450 K; (c) and (d) after annealing the surface that gave spectra b to 1100 and 1300 K.

K (see above). Annealing of the surface to 1300 K produced partial decomposition of the boron-nitrogen adlayer. At 1500 K, only a small amount of B remained on the surface with no N present.

B. Adsorption of Diborane on N/Ru(0001) Surfaces. At 450 K, diborane decomposed readily on Ru(0001) surfaces with nitrogen precoverages between 0.06 and 0.41 ML. The resulting films after a B_2H_6 exposure of 90 langmuir were rich in boron, with θ_B close to a monolayer.

Figure 8 displays N(1s) and B(1s) XPS spectra acquired after dosing 20 langmuir of B_2H_6 to a surface precovered with 0.4 ML of N at 450 K. Deposition of B induced a change in the line shape and a shift in the binding energy of the N(1s) peak. Upon annealing to 1100 K, the composition of the adlayer was 0.37 ML of N and 0.56 ML of B. The N(1s) peak position seen at 1100 K (~ 398.6 eV) is close to that observed in spectrum c of Figure 7 and to values reported for boron-nitride films that are rich in boron.³ At 1100 K, the B(1s) spectrum is characterized by the presence of a peak at ~ 190.3 eV with a broad shoulder toward lower binding energy. A similar type of spectrum has been reported for BN films that have an excess of B.³ The main peak corresponds to boron atoms in a chemical environment similar to that in boron-nitride, whereas the features toward lower binding energy correspond to boron atoms with a small number of nitrogen neighbors.³ A large fraction of boron-nitrogen adlayer was removed from the surface by annealing to 1300 K.

C. Coadsorption of Diborane and Hydrazine on Ru(0001). The synthesis of boron-nitrogen films from reaction of B_2H_6 and N_2H_4 on Ru(0001) was investigated under UHV conditions. Our results showed that films with coverages in excess of 1 ML were produced by dosing multilayers of B_2H_6 and N_2H_4 at 90 K and subsequent annealing to 450 K. The B/N atomic ratio of these films was controlled by changing the relative amounts of N_2H_4 and B_2H_6 initially dosed. Upon annealing to 1100 K, the B/N ratio in the adlayers was always equal to or greater than 1.

Thermal desorption spectra acquired after dosing hydrazine and diborane at 90 K showed evolution of N_2H_4 , B_2H_6 , NH_3 , N_2 , and H_2 . The line shapes of the spectra depended strongly on the relative amounts of B_2H_6 and N_2H_4 dosed. In general N_2H_4 and B_2H_6 multilayers desorbed between 150 and 200 K, with N_2 , NH_3 , and H_2 evolution between 220 and 450 K.

Figure 9 shows B(1s) and N(1s) XPS spectra taken after coadsorbing multilayers of B_2H_6 and N_2H_4 at 90 K. The reactants were dosed one at a time. We used the following dosing sequence: initially 1.5 ML of hydrazine were deposited on the Ru(0001) surface, followed by 1.5 ML of B_2H_6 , 1.5 ML of N_2H_4 and 1.5 ML of B_2H_6 . The peak positions seen at 90 K are in good agreement with the corresponding values for multilayers of hydrazine and diborane, suggesting that no reaction occurs at this

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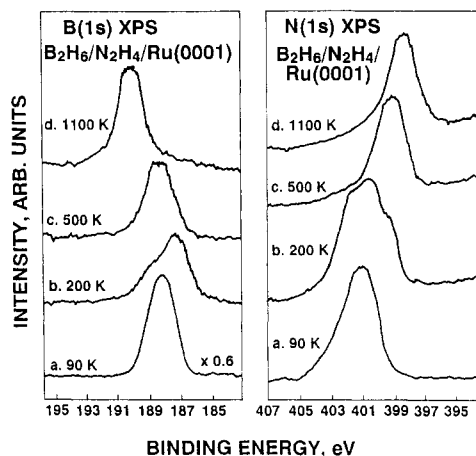


Figure 9. B(1s) and N(1s) XPS spectra for boron-nitrogen adlayers on Ru(0001) formed by reaction between hydrazine and diborane: (a) at 90 K after sequential dosing of N_2H_4 and B_2H_6 ; (b) at 200 K after desorbing the N_2H_4 and B_2H_6 multilayers; (c) after flashing to 500 K to desorb H_2 , N_2 , N_2H_4 , and NH_3 ; and (d) after annealing to 1100 K.

low temperature and that the film consists of ice layers of the reactants. Heating to 200 K induced desorption of the physisorbed N_2H_4 and B_2H_6 . The XPS spectra observed at these conditions are very different from those observed for chemisorption of hydrazine (Figure 2) or diborane (Figure 5 in ref 4) on clean Ru(0001). In particular, the N(1s) spectrum shows features that are at higher binding energy than those for physisorbed and chemisorbed hydrazine. These data indicate that there was reaction between B_2H_6 and N_2H_4 . In gas phase the reaction $2\text{NH}_3 + \text{B}_2\text{H}_6 \rightarrow 2\text{H}_3\text{NBH}_3$ is well known ($\Delta H \approx -25$ kcal/mol^{25,26}). A similar reaction may be occurring between hydrazine and diborane: $\text{H}_2\text{NNH}_2 + \text{B}_2\text{H}_6 \rightarrow (\text{BH}_3)_2\text{H}_2\text{NNH}_2(\text{BH}_3)$. The $\text{B}_2\text{-N}_2\text{H}_{10}$ species could be the precursor for the formation of the boron-nitrogen overlayers. Aminoborane ($\text{H}_2\text{B=NH}_2$) and μ -aminodiborane ($\text{H}_2\text{NB}_2\text{H}_5$) have been isolated as reaction products arising from the high-temperature pyrolysis of mixtures of B_2H_6 and NH_3 .²⁷

Appreciable changes are observed in Figure 9 after annealing the surface from 200 to 500 K. For the N(1s) features there is a decrease in peak intensity (caused by N_2 and NH_3 desorption) and a shift toward lower binding energy. Further heating to 1100 K produced B(1s) and N(1s) spectra centered at ~ 190.5 and 398.6 eV, respectively. These peak positions are close to those reported for boron nitride.^{3,24} At 1100 K, the overlayer was composed by 0.96 ML of B and 0.92 ML of N. These values were reduced to $\theta_{\text{B}} = 0.64$ ML and $\theta_{\text{N}} = 0.62$ ML upon heating to 1300 K.

In a different set of experiments, diborane and hydrazine were dosed simultaneously at a surface temperature of 450 K. In a typical dose, the partial pressures of the reactants were kept in the range from 5×10^{-8} to 2×10^{-7} Torr for 10 min. The produced boron-nitrogen overlayers presented N/B stoichiometries that varied from 0.6 to 1.8. The N in excess was removed by annealing to 1100 K. Figure 10 shows XPS spectra acquired after a simultaneous dose of 40 langmuir of B_2H_6 and 150 langmuir of N_2H_4 . At 450 K, the film showed a composition of 0.87 ML of B and 1.36 ML of N. Annealing to 1100 K produced spectra similar to those in Figure 9, and a composition of 0.84 ML of B and 0.81 ML of N. Further heating to 1300 K led to $\theta_{\text{B}} = 0.61$ ML and $\theta_{\text{N}} = 0.59$ ML.

III.3 Adsorption of Oxygen on B_xN_y Overlayers. Oxygen is a major contaminant in the synthesis of boron nitride films, reducing the thermal stability and modifying the electrical and mechanical properties of the coatings.¹⁻³ In the preceding article in this

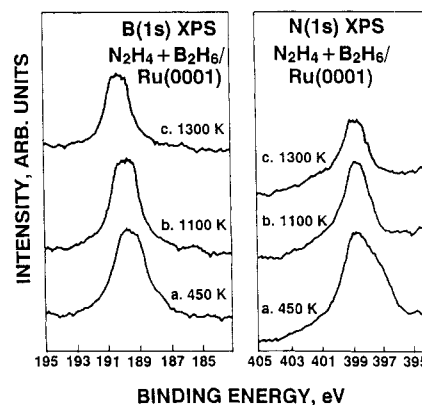


Figure 10. B(1s) and N(1s) XPS spectra for boron-nitrogen adlayers formed by simultaneously dosing diborane and hydrazine to Ru(0001) at 450 K.

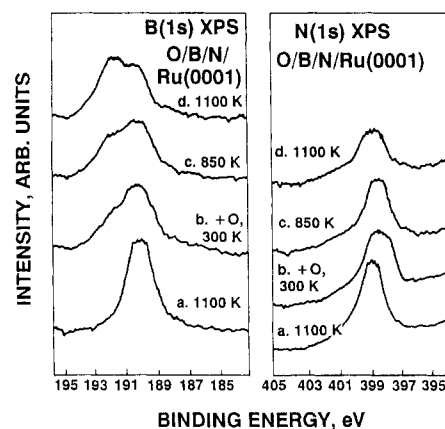


Figure 11. Effect of atomic oxygen upon the B(1s) and N(1s) XPS spectra for boron-nitrogen adlayers on Ru(0001): (a) after dosing hydrazine and diborane at 90 K and subsequent annealing to 1100 K ($\theta_{\text{B}} = 0.74$ ML and $\theta_{\text{N}} = 0.68$ ML); (b) after dosing 0.34 ML of O at 300 K; (c) and (d) after annealing the surface that gave spectrum b to 850 and 1100 K ($\theta_{\text{B}} = 0.71$ ML, $\theta_{\text{N}} = 0.31$ ML, and $\theta_{\text{O}} = 0.32$ ML).

journal, we observed decomposition of B_2H_6 on O/Ru(0001) surfaces and the formation of strong B-O bonds. The presence of boron adatoms enhanced the ability of Ru(0001) to chemisorb oxygen.⁴ Oxygen coverages in excess of 0.5 ML ($\theta_{\text{O}} = \text{saturation}$ for clean Ru(0001)²⁸) were easily obtained when O and B were coadsorbed.

In our experiments adlayers with B and N coverages above 1 ML showed a very low capacity to adsorb O_2 at temperatures between 300 and 1000 K. On the other hand when the coverage of N dropped below 1 ML, adsorption of oxygen was observed in the XPS. In those cases, oxygen reduced the thermal stability of the boron-nitrogen overlayer by making strong bonds with the B atoms that produced a weakening in the B-N bonds.

Figure 11 displays B(1s) and N(1s) XPS spectra taken after dosing 0.34 ML of oxygen to a boron-nitrogen overlayer with 0.74 ML of B and 0.68 ML of N. The adlayer was annealed twice to 1100 K before adsorbing the oxygen. The presence of this element induced a broadening in the N(1s) spectrum and the appearance of a peak around 191.5 eV in the B(1s) spectrum. Heating of the surface to 850 and 1100 K produced desorption of nitrogen (not observed before adsorption of oxygen) and an increase in the intensity of the B(1s) feature at higher binding energy. At 1100 K this feature is centered at ~ 192.0 , a value close to those reported for compounds with B-O bonds.²⁴

IV. Conclusions

(1) N_2H_4 thermal desorption spectra acquired after adsorption of hydrazine on Ru(0001) at 90 K showed peaks at ~ 185

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(multilayer state) and 280 K (monolayer state, desorption activation energy of 16.6 kcal/mol). Hydrazine decomposed extensively into NH_3 , N_2 , H, and N. B adatoms (electron-acceptor species) enhanced the bonding energy of hydrazine molecules (electron-donor species) on Ru(0001).

(2) Thermal desorption spectra from N/Ru(0001) surfaces showed N_2 evolution in a sharp peak at ~ 510 K and in a broad feature between 600 and 800 K.

(3) Boron-nitrogen adlayers with stoichiometry close to 1:1 were formed: (a) after coadsorption of B_2H_6 and N_2H_4 at 90 K, and

subsequent annealing to temperatures above 450 K, and (b) by simultaneous dosing of B_2H_6 and N_2H_4 to Ru(0001) at 450 K.

(4) For films with $\theta_N < 1$ ML, adsorbed atomic oxygen reduced the stability of the boron-nitrogen adlayers by forming strong B-O bonds.

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Registry No. B_2H_6 , 19287-45-7; N_2H_4 , 302-01-2; BN, 10043-11-5; Ru, 7440-18-8.

Fractal Surfaces of Gold and Platinum Electrodeposits. Dimensionality Determination by Scanning Tunneling Microscopy

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The structure of gold and platinum deposits grown on gold and platinum wire cathodes, respectively, by electroreduction of the corresponding oxide layers has been analyzed in terms of surface fractals by measuring the perimeter L and area A of intergranular voids. Perimeter and area were determined from scanning tunneling microscopy (STM) topographic images of the deposit surfaces. Fractal behavior, $L \propto A^{D'/2}$ with $D' = 1.5 \pm 0.1$, is found for both platinum and gold deposits. From these measurements, the fractal dimension of the surfaces was 2.5. The D' value of the gold deposits decreases by aging in the electrolyte at 325 K as a consequence of surface diffusion processes.

Introduction

The kinetics of surface reactions on metals is extremely dependent on the topography of the reacting surfaces. Real systems exhibit complicated shapes with a high degree of irregularity or disorder. In these cases fractal geometry has been useful to characterize rough surfaces in very general terms. Metal films grown under nonequilibrium conditions exhibit complicated structures and rough surfaces.¹⁻⁴ An important case is the process of metal electrodeposition either from aqueous solutions or from hydrous metal oxide layers in aqueous acid electrolytes. The first process can generate dendritic, dense radial and DLA patterns according to the growth conditions.^{2,3} The second process, although less studied, can generate thin metal films with columnar-like structures similar to those described for metal deposits grown from the vapor phase⁵ or thick metal film showing self-similar patterns.⁶ Fractal characterization of these structures is usually made in the micrometer to centimeter range so that little information is available on the fractal nature of the deposit surfaces at the nanometer level. In this paper we present an island type analysis⁷ based on determination of the perimeter L and area A of intergranular voids of metal electrodeposits measured by scanning tunneling microscopy (STM) as a method to investigate

the fractal nature of the electrodeposit surface at the nanometer level and to estimate the corresponding fractal dimension D .

Experimental Section

Gold and platinum films (thickness $\approx 10^{-5}$ – 10^{-4} cm) were prepared in 0.5 M H_2SO_4 at 298 K electroreducing the corresponding oxide layers grown on polycrystalline gold and platinum wires (length 0.4 cm; radius 0.05 cm). The electrochemical procedure for the preparation of these metal deposits has been reported elsewhere.^{5,8} The electrodeposition of the gold and platinum oxide layers was made by applying potential sweep rates of 0.02 and 0.005 V/s for gold and platinum substrates, respectively. Under these conditions the growth rate of the electrodeposit

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