Ion- and Photo-Analysis of Metal Chelate Reactions on the Semiconductor Surface

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The continuing advances in miniaturization of semiconductor devices have seriously challenged contact technology. This work explored the chemical reaction involved in the bottom-up formation of metal contacts using a linear atomic metal string chelate for CVD. The adsorption and thermal reaction of a linear dipyridylamino trichromium chelate on the GaN surface were characterized using x-ray photoelectron spectroscopy, secondary ion mass spectrometry, and thermal programmed desorption. The chelate may react with GaN at 105 K and chemisorb on the substrate surface via bonding of the chromium atom in the central metal chain after its terminal bond was disrupted. The bonding of dipyridylamino ligands to the central metal chain remained intact during chemisorption. The chromium atom string of the chemisorbed species was inclined to the surface. A change in bonding configuration of the chelate took place as the chelate dose to the substrate was increased. The chemisorbed structure was stable on the surface in the substrate temperature range between 110 K and 260 K. Some dipyridylamino ligands may be detached from the chelate at ~340 K. At a higher substrate temperature of ~540 K, additional ligands may dissociate, along with the cleavage of the chemical bond in the central metal chain.

Keywords: Metal contacts; Bonding chemistry; CVD; Nanocontact technology; Photoanalysis; Chelate orientation; Surface reaction.

INTRODUCTION

The contact technology between metals and semiconductors has drawn much attention in the optoelectronic and electronic industries.[1] Electronic devices are useless unless they are able to communicate with the outside world and with one another. The communication is done through metal contacts. As the critical structure of the integrated circuits currently shrinks in the double-digit nanometer regime, the complexity of the chemical issues related to the metal contacts on semiconductors is dramatically increased. In this regime, the signal transport may be dominated by the chemical and physical effects of atomic-size constraints in the active layers and substrates.[2] Since one of the critical issues in realizing high performance electronic devices is to achieve chemical stability with time and temperature, understanding in atomic detail of the chemical reactions involved in the formation of the metal contacts thus represents a major challenge to the forefront technology of device fabrication.

In the past, the study of the metal-surface interface has been performed either by depositing various metal halides or carbonyls to the substrate or by exposing the intended substrate to the thermal metal source. Major limitations, however, are present for the use of halides or carbonyls as starting materials in fabricating nanoelectronics. Metal halides need high temperature for conversion via the hydrogen reduction to metal films. Thermal decomposition of metal carbonyls may produce metal films of significantly high resistivity because of the film contamination by carbon and oxygen.[3]

A particular problem also arises at the contact of metal films to the compound semiconductor. When a metal is deposited to the surface of a compound semiconductor substrate, a ternary system is formed. As predicted by the phase rule, most ternary systems tend to form three solid phases in equilibrium. That is, the deposited metal may react chemically with the compound semiconductor substrate to form a three-phase system. It will not be in thermodynamic equilibrium with the substrate, unless the metal hap-

Dedicated to the memory of the late Professor Ho Tong-Ing.

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pens to form a pseudobinary with the compound semiconductor. Such a chemical reaction, however, may cause the substrate to lose part of the compound and result in the generation of defects in the interface. The device performance and lifetime may thus degrade as a function of time.

Some of the problems addressed above may be circumvented when the metal contact is formed bottom-up from linear atomic metal strings on the semiconductor, instead of top-down from the deposited metal film. With the bottom-up approach, the property of the metal contact formed will be determined mainly by the bonding chemistry rendered from individual metal strings at the contact, instead of the production process, the contamination, or the complication due to the formation of a ternary system.

In this study, the atomic-scale metal contact on the compound semiconductor will be formed by chemically depositing organometallic compounds at low temperatures compatible with advanced nanoelectronic materials or structures. The chemical deposition of organometallic compounds on the semiconductor surface is a well developed method.[4-6] This work distinguishes itself from those being done previously since the inorganic chelate of linear atomic metal strings is used in the deposition. The site-specific bonding of the metal-string chelate allows not only the strategic design of the nature of the contact, but also the investigation in detail of the bonding chemistry involved in the formation of the contact.

The linear metal-string compound used in this study is a dipyridylamino chelate of the trichromium atom string.[7-9] The chelate, tetrakis(2,2′-dipyridylamino)chromium(VI) chloride, has a central linear string comprised of three Cr atoms and terminated at both ends by Cl atoms. The central metal string is encaged by four dipyridylamino ligands, which wrap around the string helically in a syn-syn configuration.[9] Each ligand contains two terminal pyridyl groups, bridged together by one N atom. The two pyridyl groups bond separately to the two terminal Cr atoms of the string and the bridging N atom bonds to the middle Cr atom.

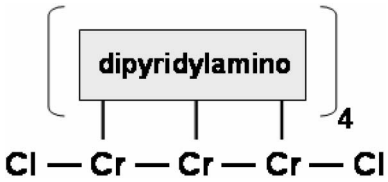

Fig. 1. Schematic of a trinuclear chromium chelate. Four 2,2′-dipyridylamino ligands wrap helically around the central linear Cr string.

EXPERIMENTAL SECTION

The semiconductor substrate used was a GaN(0001) film acquired from Cree, Inc. which had a Ga-terminated surface. They were of 4 μm thickness grown on sapphire and were undoped, with a carrier concentration of 3.7×10^{18} cm^{-3}. Prior to being placed in the analysis system, the samples were subjected to a wet-chemical cleaning process, including treatment of the surface with a 1M NaOH solution for 1 min at room temperature followed by rinsing with de-ionized water. After the treatment, the sample was clipped onto a thin tantalum sheet, which in turn was mounted on a XYZ sample manipulator using tantalum clamps. A pair of Chromel-Alumel thermocouples was spot-welded to the tantalum sheet for monitoring the sample temperature.

Once placed in the analysis system, the GaN sample surface was sputtered by high-energy ions to remove impurities on the surface. The analysis system was also equipped with a CLAM II electron energy analyzer, used for x-ray photoelectron spectroscopy (XPS) studies, a quadrupole mass spectrometer, used for static secondary ion mass spectrometry (SIMS), and a retarding field energy analyzer for low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) studies. The details of the system design are described elsewhere.[10] To inhibit the formation of metallic gallium on the GaN surface during sample cleaning, the sputtering was performed using nitrogen ions.[11] Repeated cycles of sputtering (500 eV, 0.7 μA beam current, 20 min) and annealing were carried out, with the annealing temperature of below 1050 K so as not to cause GaN decomposition in the high temperature region.[12] Sample annealing was obtained in this work by passing a high electrical current through the tantalum sheet, while cooling to 110 K was made possible by conduction from a nearby copper tank filled with liquid nitrogen.[13] A well-ordered but faceted surface was obtained, as demonstrated by a hexagonal 1x1 LEED pattern with satellite spots,[14] after sample cleaning. No oxygen and carbon contamination could be detected by AES.

Molecular evaporation of the trichromium chelate was verified by depositing in vacuum a thick film of the chelate on a stainless steel plate. Subsequent thermal gravimetric analysis and fast atom bombardment measurements

showed identical spectra to those taken before evaporation. The exposure pressure was measured with an ionization gauge and was kept below ~2×10^{-9} torr. The dose reported here is the corresponding background exposure at the sample surface and expressed as the unit of langmuir (1 L = 1×10^{-6} torr-s).

Temperature programmed desorption (TPD) experiments were conducted with the sample in line-of-sight of the mass spectrometer. To preferentially admit gases desorbing directly from the sample surface to the ionizer, this spectrometer was fitted with a stainless steel skimmer with a 0.3 cm diameter opening. For TPD measurements, the sample was placed ~0.1 in. away from the skimmer. A heating rate of ~2.5 K/s was used in all TPD experiments.

XPS studies were performed at 6 m LSGM beamline of National Synchrotron Radiation Research Center, Taiwan, with the photon energy of 250 eV. The incident angle of photons to the surface normal was 45°, and photoelectrons were collected with the analyzer normal to the sample surface. The single component spectra shown in the XPS Cl 2p plot in this article were extracted from the raw data by using a standard spin-orbit decoupling procedure with the spin-orbit energy splitting value of 1.60 eV and the branching ratio of 2:1 for Cl 2p.[15] The collected spectra were numerically fitted with the Gaussian function, after Shirley background subtraction.[16] The binding energies in the spectra refer to the binding energy of the metallic Ga $3d_{5/2}$ at 18.9 eV.[17] SIMS measurements were performed with the sample in line-of-sight of the mass spectrometer. A primary beam of Ar ions of 2-keV energy was used to bombard the sample, with the impact angle measured from the surface fixed at 45 degrees. During the measurement, the ion flux was held in the 0.5-1.5 × 10^{-9} Amp/cm^2 range.

RESULTS AND DISCUSSION

The chemical process involved in the reaction of the trinuclear chromium chelate with the semiconductor surface was investigated using SIMS.[18] Shown in Fig. 2 are the SIMS spectra taken from a GaN(0001) surface exposed at 105 K to several different doses of the trinuclear chromium chelate and its ligand, dipyridylamine, respectively. For the surface exposed to the trinuclear chromium chelate at the low dose of 0.46 L (Fig. 2a), the positive SIMS spectrum obtained was dominated by the sputter desorption of Ga^+ isotopes, measured at m/e 69 and 71, from the substrate. A number of small peaks at m/e 52, 78, 130, 172, and 222 were also identified in the spectrum. As mentioned before, there are four dipyridylamino (m/e 170) ligands in the trinuclear chromium chelate wrapping helically around the trinuclear Cr metal atom chain. Considering various mass combinations for the possible sputtered species made up from segments of the chelate under ion bombardment showed that the m/e 172 peak observed in Fig. 2a was due to the contribution from desorption of the ligand which provided two hydrogen atoms during sputtering. The mass signal observed at m/e 78 may be attributed to the pyridyl unit breaking away from the dipyridylamino ligand. The m/e 52 peak was ascribed to the emission of Cr^+ ions from the chelate-exposed surface. Small signals peaking around m/e 78, 130, 172, and 222 were also observed in the spectrum.

As shown in Fig. 2, all the SIMS peak intensities, except the Ga^+ peak intensity, increased as the chelate exposure was increased to 3.0 L. It indicated that the chelate may adsorb at increasing exposures on the sample surface at 105 K. In order to deduce the reaction process taking place on the surface upon chelate adsorption, SIMS spectra of the model compound of dipyridylamine, which is the ligand molecule of the chelate, adsorbed on the sample sur-

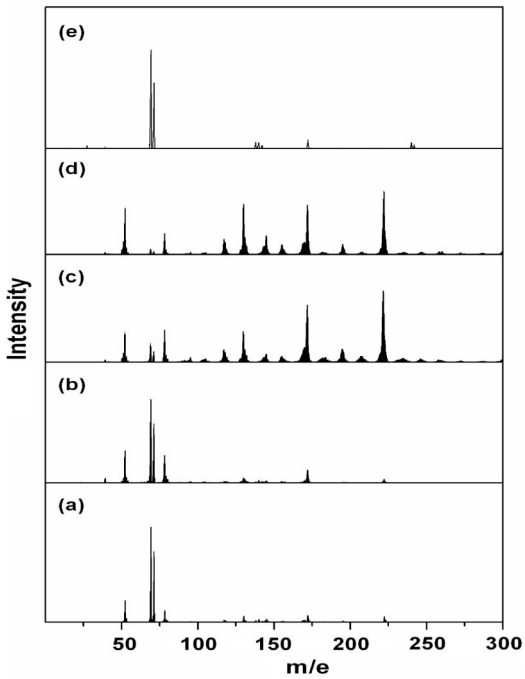

Fig. 2. SIMS spectra of a GaN(0001) surface exposed to (a) 0.46 L, (b) 1.4 L, (c) 3.6 L, (d) 5.4 L of the trinuclear chromium chelate and (e) 0.025 L of dipyridylamine, respectively. All spectra are recorded at 105 K.

face were taken for comparison with those obtained from the surface exposed to the chelate. As shown in Fig. 2e, which was normalized to the m/e 69 signal intensity of Fig. 2a, the major peaks observed in the SIMS spectrum obtained from the exposure of ligand molecules on the surface included those due to the sputtering of Ga_2 (m/e 138, 140, 142), the protonated ligand (m/e 172), and the Ga-ligand adduct (m/e 240, 242). The spectrum contains no signals from the fragments of the ligand molecule, indicating that the ligand exposure to the sample surface resulted in molecular adsorption. The observation of the m/e 240 and 242 peaks, with the intensity ratio close to that for the peaks measured at m/e 69 and 71, revealed that the ligand molecule may adsorb on the Ga site of the surface. As shown in Figs. 1a and 1b, there were no signals detected at these two m/e values from the sample surface exposed to the chelate, however. The presence of the protonated ligand and the absence of Ga-ligand adduct signal in the SIMS spectrum taken from the chelate-exposed surface indicated that the chelate structure may remain intact upon adsorption at 105 K on the sample surface.

It is known that defects such as grain boundaries are present on the GaN crystalline surface.[19,20] Upon adsorption of the trinuclear chromium chelate at low doses, the decomposition of the chelate may be induced in the presence of these defects to yield small fragments of the chelates, including possibly the pyridyl group (m/e 78), on the surface.[21,22] However, the ligands of the adsorbed chelate may be sputter desorbed from the adsorbed molecules during SIMS measurement to give the observed peak at m/e 172. The attribution of the major SIMS peaks obtained in Figs. 1a and 1b to the bombardment-induced bond rupture, due to the dissipation of the probe ion energy in the large admolecule, of the stable chelates adsorbed on the sample surface also explained the presence of the pyridyl-Cr (m/e 130) and ligand-Cr (m/e 222) adduct peaks, instead of the pyridyl-Ga and ligand-Ga peaks, in the SIMS spectrum shown in Figs. 1a and 1b. It should also be pointed out that the observation of the Cr and Cr-adduct signals in the SIMS spectrum does not imply that most chelates adsorbed on the surface were completely dissociated to expose their central metal atoms to the probe ion. The lower ionization energy of the metal atom like Cr, as compared to the ionization energy of organic species, may result in the relatively large peak intensity observed in the SIMS spectrum at m/e values related to Cr-containing species even at the surface electronic condition when the bombardment-induced Cr atom desorption is smaller than that of the organic neutrals.

Fig. 2 also shows that as the exposure of the trinuclear chromium chelate was increased to more than 3.0 L, there was a change in the SIMS intensity distribution. The relative intensities of the Cr, pyridyl-Cr, and ligand-Cr peaks increased substantially, as compared to the protonated ligand peak intensity, whereas one of the pyridyl peaks decreased. It indicated that there may be a change in the chelate adsorption behavior on the sample surface at exposures higher than 3.0 L.

In order to investigate the adsorption chemistry of the trichromium chelate on the sample surface, a photoanalysis method such as XPS was used. With this method, the bonding of the metals in the chelate at the contact with the semiconductor substrate can be investigated by examining the binding energies of their inner-shell electrons. In general, metals chemically bound to different elements or to different numbers of the same elements possess electronic configurations with the electrons outside their atomic nuclei residing at orbitals of different energy levels. Thus, the electrons being ejected from the inner-shell energy levels in XPS due to the perturbation of the incident x-ray photons will have different kinetic energies depending on the exact chemical environment the metal atoms have. By measuring the kinetic energy distribution of the inner-shell electrons emitted from the sample surface, one may then determine the chemical nature of the metals of the chelate formed at the contact.

Shown in Fig. 3 are the binding energy distributions of the electrons ejected from the Cr 3p orbital of the sample surface after it was deposited at 105 K with the trinuclear chromium chelate at the indicated doses. A broad XPS profile, with the full width at half maximum of ~2.5 eV, was obtained as the sample surface was exposed to the chelate of 0.80 L. Its intensity increased with the exposure. The fact that the XPS profile obtained from the sample, which was not a metallic substrate, was not quite symmetric indicated that there was more than one chemical state associated with the Cr atoms present in the trichromium chelate-exposed GaN system.

The presence of more than one Cr state on the sample substrate is consistent with predictions based on the molecular structure of the trichromium chelate. For the free trinuclear Cr atom string chelate, the Cr atom at the center of the string is tied to two Cr atoms, in addition to its Cr–N bonding to the N bridge atom of the dipyridylamino ligand. In contrast, the two Cr atoms on the ends of the central

metal chain in the chelate experience identical chemical environments, but ones that differ from that of the central Cr atom. Each terminal Cr atom is bound to a Cl atom on one side and to a Cr atom on the other, in addition to Cr–N bonding to the pyridyl groups of the dipyridylamino ligand. Thus, a free chelate molecule should possess two different Cr chemical states, rather than one.

The chemical states of Cr present on the substrate surface can be deduced from Fig. 3 via deconvolution of the Cr 3p XPS profile. Peak fitting of the Cr 3p profile indicated that the Cr 3p spectra obtained at doses of less than ~3.0 L could not be fitted well with only two component peaks each. The best fit of these spectra was obtained when at least three subpeaks, positioned at 45.9 eV, 44.7 eV, and 43.6 eV, respectively, were assumed in the fitting. There were thus three chemical states associated with the Cr atoms of the trinuclear chromium chelate present on the sample surface in the low dose regime of less than ~3.0 L. The result did not support the prediction, based on the molecular structure of the free chelate, that there were only two Cr chemical states present in the system if the chelate had adsorbed physically as an intact molecule on the sample substrate. The observation of three subpeaks in the Cr 3p XPS profiles obtained at low doses thus indicated that the chemical reaction of the chelate with the sample substrate may take place upon its deposition at 105 K. It led to Cr bonding chemically to the substrate and brought about a new chemical state for the bonding Cr atom, which was in a chemical environment different to those of the Cr atoms in the free chelate.

To further deduce the adsorption chemistry of the trinuclear chromium chelate on the sample surface, the XPS spectra of the electrons ejected from the Cl 2p orbital of the sample surface were measured. As shown in Fig. 4, the Cl $2p_{3/2}$ XPS peak obtained at a low dose of 0.94 L at 105 K can be fitted with two component peaks at binding energies of 198.9 eV and 200.0 eV, respectively. Both peaks grew in intensity with the dose up to 2.9 L, while the ratio of their peak areas remained roughly constant. Because the two Cl atoms in the trinuclear chromium molecule have identical bonding configurations and the chelate structure of the molecule remains intact upon adsorption at

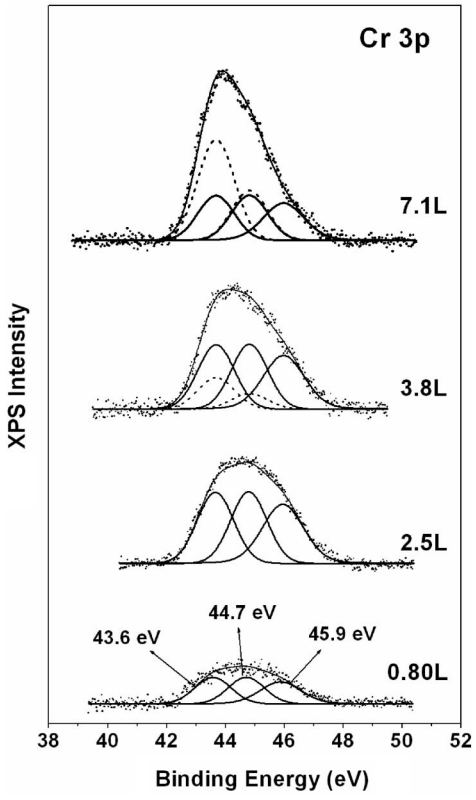

Fig. 3. XPS spectra of Cr 3p obtained from the GaN surface exposed at 105 K to the indicated doses of the trinuclear chromium chelate.

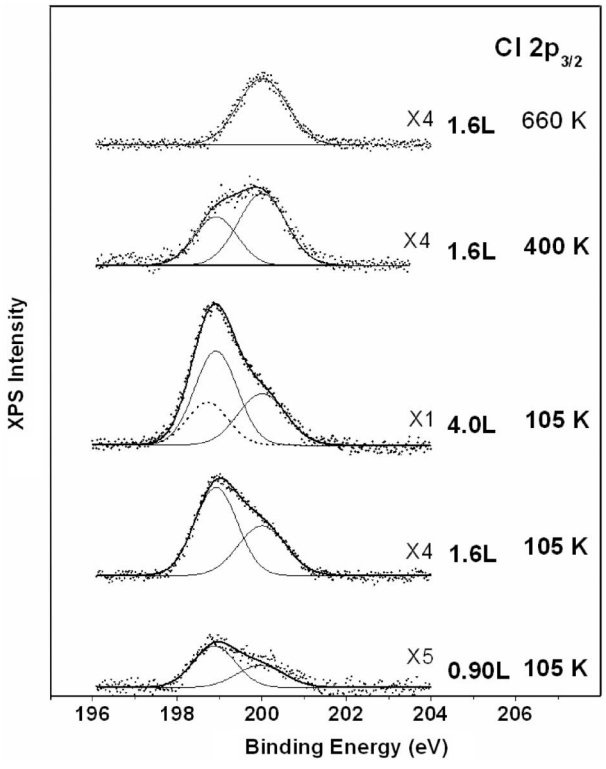

Fig. 4. XPS spectra of Cl $2p_{3/2}$ obtained from the GaN(0001) surface exposed at indicated substrate temperatures to the indicated doses of the trinuclear chromium chelate.

105 K, the observation of two features in the Cl $2p_{3/2}$ spectrum indicates that in the low dose region, some of the terminal Cr-Cl bonds of the chromium chelate adsorbed on the surface may be disrupted during the reaction to yield two different Cl chemical states. The electronegativity of Cl may cause the disrupted atom to bond on the positive site, the Ga atom, of the polar GaN surface and result in the observation of the Cl $2p_{3/2}$ subpeak measured at 200.0 eV. Because of the lower electronegativity of Cr than Ga, the subpeak observed at the lower binding energy of 198.9 eV in Fig. 4 may be associated with the undisrupted Cl atom remaining bonded to the end of the Cr atom chain in the trichromium chelate.

Both Fig. 3 and Fig. 4 reveal that the adsorbed chelate at 105 K was not oriented parallel to the surface. For the chelate to chemisorb on the sample surface with its Cr atom string oriented parallel to the surface, the two terminal Cr atoms of the string should have given rise to XPS signals at the same binding energy, resulting in a Cr 3p XPS profile comprised of only two component peaks. Three subpeaks were observed, however, in the Cr 3p XPS spectra (Fig. 3) measured at low exposures of less than ~3.0 L. In addition, the peak areas of the three Cr subpeaks were about equal in each of the spectra obtained at low exposures. It revealed that for each adsorbed chelate, only one of the two terminal Cr-Cl bonds in the trichromium chelate was broken upon adsorption and that all the adsorbed chelate anchored to the sample surface with one end of the string bonding to the surface and the other remaining free.

As shown in Fig. 3, further increasing the trichromium chelate dose to more than ~3.0 L caused an increase in Cr 3p peak intensity of only two of the three subpeaks observed at low doses. The presence of two additional component peaks, with the ratio of the peak areas of 2:1 and at high doses of more than ~3.0 L, indicated that the chelates of high doses may adsorb with their string axis oriented parallel to the surface. With such a bonding configuration, the trinuclear chromium chelate adsorbed on the sample surface may not interact with the substrate strongly enough to cause bond breakage. It thus led to the observation in Fig. 4 of the growth with the dose of the Cl 2p intensity for the 198.9-eV peak only, as the trichromium chelate exposure was higher than ~3.0 L.

Molecular adsorption of the trinuclear chromium chelate on the sample surface may thus start to take place on top of the first adsorbate layer at high exposures of more than ~3.0 L. It also caused the large change in the SIMS intensity distribution observed between 1.4 L and 3.6 L in Fig. 2.

The small peak intensity observed in Fig. 2 at m/e 78, assigned as due to the sputter desorption of pyridine, as compared to other peak intensities obtained at high exposures is, however, very interesting. As mentioned before, the chelate structure of the trichromium chelate, in which the dipyridylamino ligand, and its pyridyl groups, wraps helically around the central atom chain, remained undisturbed during chemisorption. The Cr-N bond holding the pyridyl group of dipyridylamino to the Cr axis was mostly concealed inside the molecule when the trichromium chelate was adsorbed at high exposures with the central metal axis oriented parallel to the surface. The incident ions impinging on the sample during SIMS measurements may not be able to cause the bond cleavage of the Cr-N bond to release the pyridyl group easily, because the bond is not openly exposed to the incident ions. In addition, the pyridine ions, released from its binding to the chromium central axis by the incident ion, may not be able to easily find its way out to get to the SIMS detector, because of the presence of neighboring groups of atoms in the helically wrapped structure of the trichromium chelate which remained bonding together during the detection. The intensity of the m/e 78 signal observed in the SIMS spectrum shown in Fig. 2 was thus expected to be relatively low at high exposures of the trichromium chelate, as compared to the sputter intensity of other species measured. In comparison, the Cr-N bond between the top terminal Cr atom in the chromium chain and the pyridyl group of the dipyridylamino ligand is more exposed to the probe ions for cleavage when the trichromium chelate was adsorbed at low exposures of less than 3.0 L with its molecular axis tilted away from the surface. The tilted configuration also facilitated the pyridine ions formed from bond disruptions (of the top Cr-N bond and of the pyridine-N bond) to reach the mass spectrometer, which was configured normal to the sample surface in the experiment, because of the relatively less obstruction.[23,24] Since there are four pyridyl groups, each associated with one dipyridylamino ligand, bonded to the top Cr atom of the central metal chain for each, the trichromium chelate tilted away from the surface; the sputter yield of the pyridine ions was higher than that of other species sputtered from the trichromium chelate adsorbed at low exposures on the surface.

The chemical process involved in the thermal reaction of the trinuclear chromium chelate on the GaN(0001)

surface was investigated using TPD. Fig. 5 shows the TPD spectra taken at m/e 52 and m/e 170, respectively, from the sample surface exposed at 105 K to the chelate of 0.8 L to 3.9 L. At a low dose of 0.8 L, the desorption feature in the m/e 52 TPD curve showed the peak temperatures of desorption occurring at ~340 K and ~540 K. The intensity of both peaks increased as the dose was increased. Comparing the m/e 52 and m/e 170 TPD spectra revealed a similar desorption profile at ~340 K. Since m/e 52 was one of the fragments that was produced from the ligand molecule in the electron-impact ionizer installed in the TPD spectrometer, the observed similarity in the desoprtion profile indicated that the m/e 52 desorption peak observed at ~340 K may be attributed to the fragmentation of the dipyridylamino ligand (m/e 170) of the chelate. Since the TPD spectra measured at different m/e values all showed negligible signals at substrate temperatures of less than ~340 K, thermal decomposition of the trinuclear chromium chelate thus started on the sample surface at or below ~340 K via the detachment of the ligand.

Figs. 4 and 5 also showed that at substrate temperatures between ~340 K and ~540 K, further decomposition of the chelate took place, which led to the increase in population of the disrupted Cl on the surface (Fig. 4) as well as

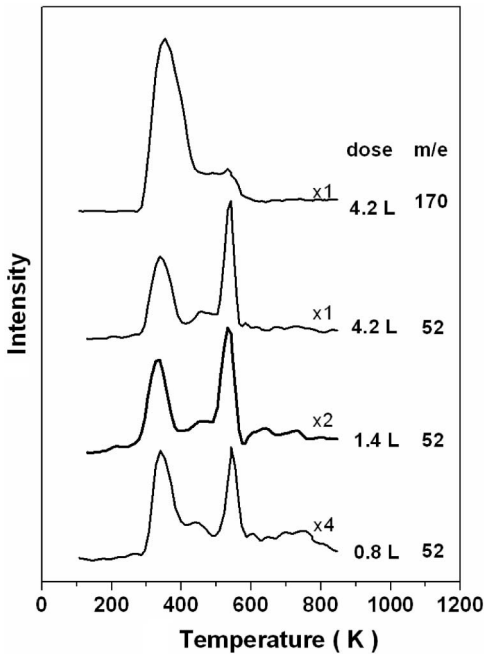

Fig. 5. TPD spectra taken at m/e 52 and m/e 170, respectively, from the GaN(0001) surface exposed at 105 K to the indicated doses of the trinuclear chromium chelate.

the desorption of species containing m/e 52, possibly Cr (Fig. 5). Fig. 4 shows that all the ligands were detached from the chromium chain of the chelate at 660 K. The larger increase at higher exposure in intensity shown in Fig. 4 of the high-temperature peak than that of the low-temperature one indicated that more than one m/e 52 species may be desorbed at ~540 K. The detachment may thus occur along with the cleavage of the Cr-Cr bond, since one of the possible m/e 52 species is Cr.

CONCLUSIONS

A dipyridylamino-chelated linear trichromium complex was employed as a model chelate to explore the reaction chemistry involved in the bottom-up formation of metal contacts on the compound semiconductor substrate. The trichromium chelate did not decompose on the GaN surface at 105 K, except that the terminal Cr-Cl bond of the chelate was disrupted. Ion incidence during SIMS measurements, however, may cause the desorption of pyridine and dipyridyl amine from the adsorbed chelate due to bond rupture via the dissipation of the incident ion energy in the large admolecule of the chelate. The disruption of one of the two terminal Cr-Cl bonds at low doses upon the chelate adsorption led to chemisorption of the chelate on the GaN surface and the anchoring of the trinuclear chelate on the sample substrate with its central metal axis tilted away from the surface. The adsorbed chelate remained structurally intact on the GaN surface at room temperature. A chemisorption layer of metal strings is formed on GaN at ~3.0 L. At high doses of more than ~3 L, the trinuclear chromium chelate adsorbed physically on top of the chemisorption layer. Most of the physisorbed trichromium chelates may be inclined to the surface, with their central metal chains oriented parallel to the surface. As the substrate temperature was increased, some ligands may be detached and desorbed from the adsorbed chelate at ~340 K. The detachment may also occur at 540 K, even though no species was desorbed between ~340 K and ~540 K. It may be accompanied by the cleavage of the Cr-Cr bond.

ACKNOWLEDGMENTS

This work was supported by ROC National Science Council (NSC94-2113-M002-032, NSC94-2120-M-002-

010). The authors gratefully thank Prof. Shi-Ming Peng for providing the trichromium chelate sample. They are grateful to Drs. Wei-Hsiu Hung and Yaw-Wen Yang of the NSRRC for allowing us to use their instruments. The synchrotron radiation beam time allocated to this work by the NSRRC is also acknowledged.

Received June 19, 2006.

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