Surface Reactions of Linear Atomic Metal Wire Complexes

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ABSTRACT

The communication among nanostructures and between these structures and the outside world becomes very critical as the key features in electronics devices continue to shrink in the double-digit nanometer regime. To explore the possible formation of molecular metal wires by CVD of organometallic complexes, the present work studies the adsorption and the thermal reaction, on the gallium arsenide surface, of the complex which contains the linear atomic metal chain wrapped helically by four ligands. Studies using synchrotron radiation-induced XPS, SIMS, and TPD showed that the pyridylamino trinuclear chromium chelate may adsorb at 105 K on the sample surface with the chelate structure remaining intact. The terminal bond of Cl to the metal chain was cleaved upon adsorption and the Cl surface population increased with the exposure. Molecular adsorption of intact chelates took place at exposures of more than saturation coverage. Increasing the substrate temperature to ~340 K caused the detachment of one of the four ligands from the chelate. Disruption of the chromium string occurred at 540 K, which led to desorption of chromium-containing species. The chemical bonding and the reaction chemistry involved in the formation of the linear metal atom wire are discussed.

Keywords: nanowire, linear atomic metal chain, chemical vapor deposition, surface reaction, metal-semiconductor chemistry

1 INTRODUCTION

In the last two decades, the continued miniaturization of electronic and optoelectronic devices has motivated a worldwide extensive research effort on low-dimensional materials. Along with the development of novel methods to prepare these materials, there is also a great need in understanding the chemistry and physics involved in the preparation. In particular, understanding the chemical reaction and bonding involved in the synthesis of the one-dimensional nanostructures, such as nanowires, nanorods, and linear atom chains, poses exciting challenges from both fundamental and application points of view.

In order to prepare conducting wires in the nanometer scale, various experimental approaches have been developed. Among them, the laser-assisted catalytic growth [1] method is a straightforward approach. It allows a composite target, consisting of a catalyst and the material of interest, to be laser-ablated in a heated flow tube. Clusters generated by laser then grow to form nanowires when they become supersaturated.

Scanning the voltage-applied tip over the surface can also be utilized to create lines of dangling bonds [2] and thus nanowires on the surface. For example, silicon conductive wires were produced by selectively desorbing H atoms from a fully hydrogenated Si(100) surface. It was demonstrated [2] that an OR gate could be formed using these dangling-bond wires.

The superlattice nanowire pattern transfer process [3] was also developed to synthesize high density nanowire arrays. In this process, the molecular beam epitaxy technique was employed to grow alternating layers of the gallium arsenide/aluminum gallium arsenide superlattice on the gallium arsenide substrate. Hydrofluoric acid was then used to selectively etch the aluminum gallium arsenide layers to a certain depth. Subsequently, metal wires were evaporated onto the top of the gallium arsenide layers while the superlattice was oriented at a certain angle with respect to the metal vapor flux. The resulting superlattice was then attached to an adhesive layer on silicon and etched to release metal wires. The nanowires fabricated using this process were well aligned [3].

Other nanowire synthesis strategy includes the use of a selective electrodeposition method [4]. The method allows metals to be deposited onto the cleaved edge of a semiconductor wafer onto which extremely thin layers of various dopant levels have been grown by molecular beam epitaxy. During electrodeposition, electrons drop from the heavily doped layer into an undoped layer because of the lineup of the particular conduction band and valence band in this modulation-doped structure. Thus, the atomic precision of the grown semiconductor layers is converted in this method to the fabrication of metallic nanowires, and ultrathin metal wires may be produced.

Since the electronic and optoelectronic devices produced nowadays rely frequently on the process of chemical vapor deposition, it is of interest to explore if conducting nanowires, especially in the form of atomic wires, may also be synthesized via the chemical vapor deposition approach on the semiconductor surface. Typically, chemical vapor deposition allows a metallic thin layer to be formed on the substrate by exposing the intended substrate surface to the thermal metal source or by depositing organometallic compounds on the surface [5]. The problem associated with such a thin-layer synthesis strategy for atomic metal wire formation is that the metal particles in contact with the surface are mostly either in the form of individual atoms or clusters. It is expected that,

instead of forming a linear nanostructure, these particles will be distributed randomly on the isotropic surface.

To circumvent the problem, oligonuclear metal-chain complexes are employed in this study as nanowire precursors. A variety of metal string chelates, which have an extended metal-metal bond supported by oligo-α-pyridylamino ligands, have been successfully synthesized by S. M. Peng, et al. [6]. The success makes our strategy of forming on the solid surface linear metal wires of the single-digit angstrom dimension a viable one, since in these chelates, the ligands bind metal ions in a linear fashion. Exploring different aspects of the interaction and bonding involved in the reaction of the oligonuclear metal string complexes on the semiconductor surface holds the promise for understanding the fundamental processes taking place at the interface between metals and semiconductors. It may open up the possibility of experimentally examining the interaction of one-dimensional metal bonds with the solid surface.

2 EXPERIMENTAL

The specific type of chelates used in this study was a trinuclear chromium atom chain complex, tetrakis(2,2'-dipyridylamino)chromium(VI) chloride. The complex had a central linear chain comprised of three Cr atoms and terminated at both ends by Cl atoms. The central metal chain was encaged by four dipyridylamino ligands, which wrapped around the chain helically in a syn-syn configuration. Each ligand contained two terminal pyridyl groups, bridged together by one N atom, and had the hydrocarbon portion of the group pointing away from the central metal chain. The two pyridyl groups bonded separately to the two terminal Cr atoms of the chain and the bridging N atom bonded to the middle Cr atom.

The experiments were performed in two different ultrahigh vacuum analysis systems. One of them was pumped by a turbomolecular pump, with a base pressure of 1×10^{-10} torr achieved after baking out. The details of the system design were described elsewhere [7]. The vacuum of the other system was maintained by an ion pump and a titanium sublimation pump. The system was used for XPS studies.

A Ga-terminated, un-doped GaN(0001), acquired from Cree, Inc. was used as the substrate. Following a wet-chemical cleaning process, the substrate surface was sputtered by nitrogen ions after it was placed under ultrahigh vacuum to ensure that as less metallic gallium was formed [8]. Repeated cycles of nitrogen ion 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 [9]. A hexagonal 1x1 LEED pattern with satellite spots was obtained after sample cleaning, indicating the presence of a well-ordered but facetted surface. No oxygen and carbon contamination could be detected by AES.

Metal string chelates were admitted via a Knudsen cell deposition source onto the sample surface. Molecular evaporation of the trichromium complex was verified by depositing in vacuum a thick film of the complex on a stainless steel plate. Subsequent TGA and FAB measurements showed identical spectra to those taken before evaporation. The exposure pressure was measured with an ionization gauge and was kept below ~2 x 10^{-9} torr. The dose reported in this study is the corresponding background exposure at the sample surface and expressed on the unit of langmuir (1 L = 1 x 10^{-6} torr-s).

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 within the 0.5-1.5 x 10^{-9} Amp/cm^2 range. TPD experiments were conducted with the sample placed ~0.1 in. away from the skimmer mounted on the mass spectrometer. A heating rate of ~2.5 K/s was used in all TPD experiments. XPS studies were performed at 6m 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 collected spectra were numerically fitted with the Gaussian- Lorentzian function, after Shirley background subtraction. The binding energies in the spectra are referred to metallic Ga $3d_{5/2}$ at 18.9 eV [10].

3 RESULTS AND DISCUSSION

The chemical process involved in the reaction of the trichromium chelate on the GaN(0001) surface was investigated using SIMS. Shown in Fig. 1 are the SIMS spectra taken from a GaN(0001) surface exposed at 105 K to several different doses of the trichromium chelate and its ligand, dipyridylamine, respectively. For the surface exposed to the trichromium chelate at the low dose of 0.45 L (Fig. 1a), the positive SIMS spectrum obtained was dominated 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 trichromium 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. 1a was due to the contribution from desorption of the ligand which obtained 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 complex-exposed surface. Small signals peaked around m/e 78, 130, 172, and 222 were also observed in the spectrum.
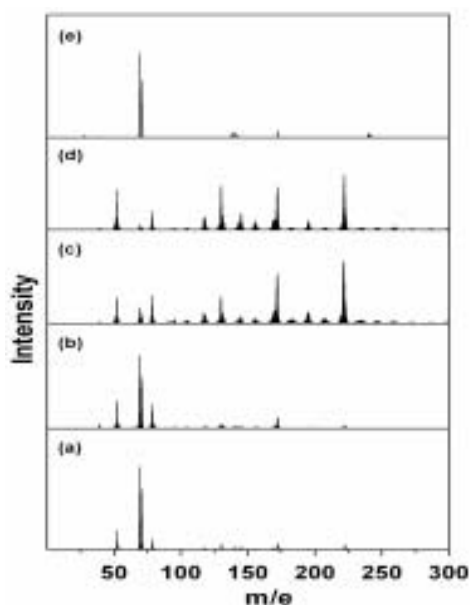
Figure 1: SIMS spectra of a GaN(0001) surface exposed to (a) 0.46L, (b) 1.4L, (c) 3.6L, (d) 5.4L of pyridylamino trichromium chelate and (e) 0.025L of dipyridylamine, respectively. All spectra are recorded at 105 K.

As shown in Fig. 1, all the SIMS peak intensities, except the Ga^+ peak intensity, increased as the chelate exposure was increased to 3.0L. It indicated that the chelate may adsorb at increasing exposures on the sample surface at 105 K. In order to deduce the reaction process taken 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 surface were taken for comparison with those obtained from the surface exposed to the chelate. As shown in Fig. 1e, which was normalized to the m/e 69 signal intensity of Fig. 1a, 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. The ligands of the adsorbed chelate, however, 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.

As the chelate exposure was increased to more than 3.0L, 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 the one of the pyridyl peak decreased. It indicated that there may be a change in the chelate adsorption behavior on the sample surface at the exposure higher than 3.0L.

The adsorption chemistry of the trichromium complex on the sample surface was further investigated using XPS. As shown in Fig. 2, the Cl $2p_{3/2}$ XPS peak obtained at low
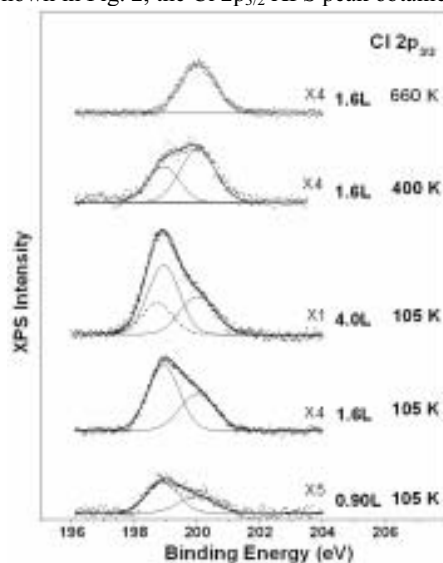

Figure 2: XPS spectra of Cl $2p_{3/2}$ obtained from the GaN(0001) surface exposed at indicated substrate temperatures to the indicated dosages of the trichromium chelate.

chelate exposure 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

chelate exposure up to 2.9 L, with the ratio of their peak areas remained roughly constant. Because the two Cl atoms in the chelate molecule have the identical bonding configuration and, as discussed above, the chelate structure of the molecule remains intact upon adsorption at 105 K, the observation of two features in the Cl $2p_{3/2}$ spectrum indicates that in the low exposure region, some of the terminal Cr-Cl bonds of the 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. 2 may be associated with the undisrupted Cl atom remaining bonded to the end of the Cr atom chain in the trichromium chelate.

As shown in Fig. 2, additional exposures of the chelate higher than 3.0 L did not contribute to the XPS intensity of Cl $2p_{3/2}$ at 198.9 eV and 200.0 eV. Instead, it caused the intensity at the binding energy (198.7 eV) near to the one assigned to the disrupted Cr-Cl bond to increase continuously. Since the small difference in binding energy for the XPS intensity measured at 198.9 eV and 198.7 eV is insignificant, molecular adsorption of chelates may start to take place on top of the first adsorbate layer at high exposures. The molecular adsorption of chelates at the exposures of larger than 3.0L also caused the large change in the SIMS intensity distribution observed in Fig. 1.

The chemical process involved in the thermal reaction of the trichromium complex on the GaN(0001) surface was investigated using TPD. Fig. 3 represents the TPD spectra taken at m/e 52 and m/e 170, respectively, from the sample
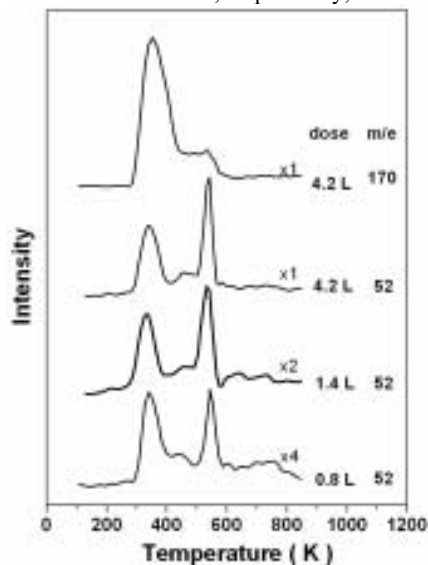

Figure 3: TPD spectra taken at m/e 52 and m/e 170, respectively, from the GaN(0001) surface exposed at 105 K to the indicated doses of pyridylamino trinuclear chromium chelate.

surface exposed at 105 K to trichromium complex of 0.8 L to 3.9 L. At low exposure 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 exposure was increased. Comparing the m/e 52 and m/e 170 TPD spectra revealed similar desorption profile at ~340 K. Since m/e 52 was one of the fragments that may be produced from the ligand molecule in the electron-impact ionizer installed in the TPD spectrometer, the observed similarity indicated that the m/e 52 desorption peak observed at ~340 K may be attributed to the fragmentation of the ligand (m/e 170). 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 trichromium chelate thus started on the sample surface at or below ~340 K via the detachment of the ligand.

Figs. 2 and 3 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. 2) as well as the desorption of species containing m/e 52, possibly Cr (Fig. 3). Fig. 2 showed that all the ligands were detached from the metal chain at 660 K. The larger increase at higher exposure in intensity shown in Fig. 3 of the high-temperature peak than that of the low-temperature one indicated that more than one m/e 52 particle may be present in the species desorbed at ~540 K. The detachment thus occurred along with the cleavage of the Cr-Cr bond.

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