09-9; $(PMe_3)Mo(CO)_5$, 16917-96-7; $(PMe_3)W(CO)_5$, 26555-11-3; $(P(NMe_2)_3)Cr(CO)_5$, 15137-66-3; $(P(NMe_2)_3)Mo(CO)_5$, 14971-43-8; $(P(NMe_2)_3)W(CO)_5$, 19976-82-0; $(P(OEt)_3)Cr(CO)_5$, 18461-32-0; $(P(OEt)_3)Mo(CO)_5$, 15603-75-5; $(P(OEt)_3)W(CO)_5$, 23306-43-6; $(P(OMe)_3)Cr(CO)_5$, 18461-34-2; $(P(OMe)_3)Mo(CO)_5$, 15631-20-6; $(P(OMe)_3)W(CO)_5$, 23306-42-5; $(PF_3)Cr(CO)_5$, 18461-42-2; $(PF_3)Mo(CO)_5$, 15322-05-1; $(PF_3)W(CO)_5$, 18461-47-7.

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Matrix-Isolation Spectroscopy of Aluminum, Copper, and Nickel Hydrides and Deuterides Produced in a Hollow-Cathode Discharge

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By use of the technique of matrix-isolation spectroscopy in conjunction with a hollow-cathode sputtering source the infrared-active vibrations of the diatomic hydrides and deuterides of aluminum, copper, and nickel have been directly observed. The metal hydride and deuteride vibrations at 14 K in an argon matrix occurred as follows: AlH, 1593 cm^{-1}; AlD, 1158 cm^{-1}; CuH, 1882 cm^{-1}; CuD, 1356 cm^{-1}; NiH, 1906 cm^{-1}; NiD, 1374 cm^{-1}.

I. Introduction

Recent interest in the possible production and detection of metal hydrides and deuterides arising from physical/chemical sputtering of metals by energetic reactive ion beams is related to the plasma first-wall interactions envisioned to occur in thermonuclear reactors. Sputtering of the first wall by ions and/or neutrals escaping from the plasma can lead to serious first-wall erosion as well as plasma contamination problems. Therefore, the qualitative and quantitative detection of the sputtered products resulting from bombardment of a metal surface by energetic hydrogen and deuterium ions is essential to ascertain the extent of these problems and the possible solutions thereof.

A convenient method for producing diatomic metal hydride and deuteride molecules would also be useful for a detailed examination of the elementary steps involved in catalytic reactions. Recent work on matrix-isolated ethylene[1a] as well as nickel- and platinum–ethylene complexes[1b] has shown the close relationship between the spectroscopic properties of matrix-isolated complexes and the spectroscopy of chemisorbed species on metal surfaces. To investigate intermediates in catalytic hydrogenation reactions, the program would be to matrix-isolate metal hydrides together with ethylene for example and to search for reaction products on the way to ethane. The hollow-cathode discharge method for the production of metal hydrides has some advantages over the more conventional method using thermally generated H or D beams. As will become apparent, the discharge method also appears to have some disadvantages, particularly with regard to the large M/MH ratios observed in the matrices.

The technique and utility of matrix-isolation spectroscopy has been well documented in the literature[2-5] demonstrating that it is a viable technique for the optical study of atomic and molecular (stable or unstable) species. Hollow-cathode sputtering sources where the metal atoms are sputtered from the surface of the cathode by a low-energy plasma and subsequently excited in the discharge to produce an atomic spectrum have been used for many years.[6] If small amounts of a reactive gas are added to the discharge, molecular species formed by reactions with the sputtered metal atoms can occur.[7-9] In this paper, the technique of matrix-isolation spectroscopy has been utilized to detect by infrared absorption the formation of aluminum, copper, and nickel diatomic hydrides and deuterides produced in a hollow-cathode cathode discharge. This technique permits, at present, the qualitative determination of the sputtered products resulting from a low-energy reactive plasma interaction with a metal surface using UV–visible and infrared absorption detection of the matrix-isolated sputtered species.

II. Experimental Section

A cross-sectional view of the hollow-cathode sputtering source and matrix-isolation collection assemblies is shown in Figure 1. The hollow-cathode sputtering source is similar to one which has been previously used in our laboratory;[9] the present source has been modified for easier use and reliability. A Cryogenic Technology, Inc., Model 21 closed-cycle helium refrigerator (b) enclosed by a stainless steel

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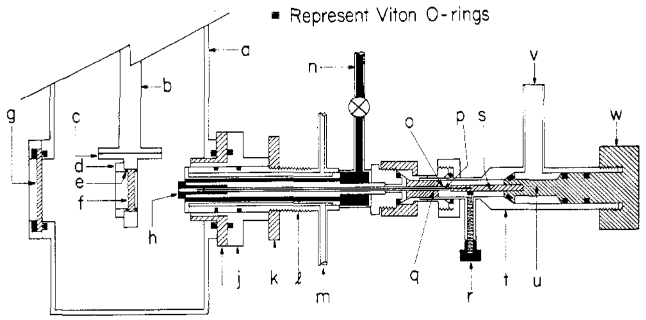

Figure 1. Cross-sectional view of matrix-isolation hollow-cathode sputtering device. See text for explanation of components.

vacuum chamber (a) is mated to a by means of a Viton O-ring sealed vacuum flange (not shown) which also provides an O-ring seal which can be used to rotate the refrigerator 90° from the position shown in Figure 1 to permit study of the matrix by transmission optical spectroscopy. This top flange assembly also has a vacuum port and valve for evacuation of the entire assembly. There are also two window assemblies (not shown) which are used in the transmission spectroscopic studies and consist of KCl or CsI windows 48 mm in diameter × 3 mm in thickness sealed to a by Viton O-rings or brass retaining rings. An OFHC–copper deposition plate holder (c) is bolted to the second-stage cold station of the refrigerator using an indium gasket for thermal contact. The deposition plate (f) is either a KCl or CsI window 25 mm in diameter × 3–4 mm in thickness which is retained in the deposition plate holder (c) by an OFHC–copper retaining ring (d) bolted to c using indium gaskets (e) on both faces of the optical window. An OFHC–copper heat shield (not shown), which is in thermal contact with the first cold stage of the refrigerator (40–80 K), surrounds the second cold stage and deposition plate. This shield has two circular openings to allow for matrix deposition and observation of the hollow-cathode discharge. Temperature measurement was accomplished using a 0.07 atom % Fe doped Au vs. chromel thermocouple clamped to the deposition plate holder. A quartz window (g) is also available for observation of the hollow-cathode discharge by a Perkin-Elmer E-1 grating monochromator equipped with photoelectric detection. The measured electronic emission spectra could then be used to optically determine the atoms and/or molecules present in the discharge.

The hollow-cathode support (l) is drilled and tapped (6-32 THD) to accept the cathode (h) made from the metal to be studied. The cathode is 28 mm long, threaded on its outer circumference (6-32 THD), and has a central hole along its axis 2.5 mm in diameter. The cathode support (l) is water cooled by internal water passages through tubes (m) and is in turn supported by a flange (j) which is sealed to a by means of Viton O-rings. The fastening screws are insulated by Teflon bushings. An intervening Teflon spacer (i) between a and j is also used for electrical insulation. The cathode support (l) may be linearly translated with respect to the deposition plate (f) by rotation of a brass threaded ring (k); two Viton O-rings provide the vacuum seal. A machined Teflon plug (q) provides a gastight seal around a 2-mm o.d. × 1-mm i.d. quartz tube (o). The quartz tube is used to insulate the 0.030-in. platinum wire anode (p) so that the plasma discharge only occurs where the platinum anode protrudes out of the quartz tube at a point inside the cathode. This point is usually at the middle of the metal cathode. The platinum anode is in turn fastened inside a brass rod (s) supported by a Kel-F stopcock plug (u). The position of the platinum anode (p) is adjusted by the stopcock knob (w). The discharge gas enters through the inlet (v) of the modified glass stopcock (t). The stopcock also acts as a vacuumtight seal by closing the stopcock valve (u) when the discharge and matrix deposition is terminated. The electrical connection to the platinum anode is accomplished by a spring-loaded electrode (r) in contact with the brass rod (s). The vacuum seal is provided by a glass to Kovar seal with a Viton O-ring vacuum compression fitting. In those experiments referred to as "dual-flow" a mixture of matrix gas (in this case argon) and reactive gas (in this case hydrogen or deuterium) was inlet to the system through inlet n. The gas then flows into a plenum chamber (shown as the black area inside the cathode support assembly in Figure 1) and exists through eight holes at the end of the cathode support assembly directly facing the deposition plate (f). In this manner, with only the inert gas flowing through the discharge (via inlet v) the reactive gas (via inlet n) is not present in the cathode discharge but may react with the sputtered metal atoms at the surface of the deposition plate (f). The gas flow (usually 5–10 mmol/h) was controlled by a Granville-Phillips Series 203 variable-leak valve and the flow rate was measured by a Teledyne Hastings-Raydist ALL-5 mass flowmeter and a H-5 mass flow transducer. Inlets n and v were connected to separate liquid nitrogen trapped oil-diffusion pumped gas manifolds through the mass flowmeters and leak valves. Gas mixtures were prepared by standard manometric procedures. All metals used to fabricate the cathodes were 99.5+% pure and all gases were Matheson research grade used without further treatment.

The external electrical connections were made to the cathode by the cooling water inlet m and to the anode by electrode assembly r. The high-voltage power supply was used at an applied voltage of 400–600 V; the current ranged from 40 to 90 mA. Before each matrix deposition the entire assembly was evacuated to 1×10^{-7} Torr or lower by a liquid nitrogen trapped oil-diffusion pump (the closed-cycle refrigerator was not operating during this period). At the end of this period the hollow-cathode source was operated for approximately 15 min to remove oxide films from the interior cathode surface. The deposition plate was rotated 90° from the position shown in Figure 1 during this discharge cleaning of the cathode. The closed-cycle refrigerator was then turned on and allowed to cool the deposition plate to 14 K. Once cooled, the deposition plate was then positioned opposite the hollow-cathode assembly and the matrix deposited after the discharge was restarted. During the deposition and operation of the hollow-cathode the assembly was also being continuously pumped by a liquid nitrogen trapped oil-diffusion pump to remove hydrogen or deuterium which was not trapped in the argon matrix at 14 K. The deposition times varied from 1 to 3 h for the results reported here.

The infrared transmission spectra were taken with a Beckman IR-12 spectrometer operated in the variable-scale expansion mode. The frequency uncertainty in the infrared spectra is about 0.5 cm^{-1} and the resolution is about 2 cm^{-1}. The only bands observed in the infrared spectra were those of the diatomic metal hydrides or deuterides discussed below and occasionally bands which could be attributed to H_2O, D_2O, CO_2, and CO molecular impurities resulting from outgassing of the unbaked vacuum chamber or from chemical reaction occurring in the discharge. Blank experiments were performed wherein the details of the experiment were the same as above except the discharge was not operated. Only the impurity bands were observed, their intensity being dependent on how long the Dewar was pumped before operation of the refrigerator (for the water bands, the ambient humidity present when the Dewar was exposed to air for periodic servicing also influenced their intensity).

III. Results and Discussion

Representative infrared transmission spectra with Al as the cathode and with gas mixtures of hydrogen and deuterium with argon are shown in Figures 2 and 3. Figure 2 is for an Al cathode with 1% H_2 in Ar as the discharge gas. The peak observed at 1593 cm^{-1} was the only band observed in the infrared spectrum (450–4000 cm^{-1}) besides the ν_2 bending mode of H_2O shown in Figure 2 and low-intensity CO_2 and CO impurity bands. With 1% D_2 in Ar the band at 1593 cm^{-1} was not present but a band at 1158 cm^{-1} appeared (Figure 3). The band at 1180 cm^{-1} is due to the ν_2 band of D_2O impurity formed in the discharge. Previously measured gas-phase vibrations (derived from electronic molecular spectra) have been reported at 1624.4 and 1181.7 cm^{-1} (including anharmonic corrections) respectively for AlH and AlD. The vibrational bands we observed and have ascribed to AlH and AlD are shifted to lower frequencies by 31.4 and 23.7 cm^{-1} for AlH and AlD, respectively. For most molecules observed by matrix-isolation infrared spectroscopy the shift is similarly to lower frequencies due to perturbation of the isolated species by the matrix. However, in the recent work of Van Zee, Seely, and Weltner[11] on the matrix isolation of YbH (YbD), the IR band due to YbH was slightly shifted to higher frequency.

The AlH/AlD ratio of the gas-phase frequencies including the first-order anharmonic correction (ν is the observed frequency)

$$\nu_g = \omega_e - 2\omega_e x_e$$

Table I. Vibrational Frequencies as Measured by Infrared Analysis of Matrix-Isolated Diatomic Hydrides and Deuterides of Al, Cu, and Ni Compared with Values Determined by Gas-Phase Electronic Emission Spectra

cathode; discharge gas	ν_g,[a,d] cm^{-1}	ν_m,[b] cm^{-1}	$\nu_g - \nu_m$	ν_g^H/ν_g^D	ν_m^H/ν_m^D
Al; 1% H_2 in Ar (AlH)	1624.4 (1682.6 − 2 × 29.1)	1593 (1647.9 − 2 × 27.5)	31.4		
				1.375	1.376
Al; 1% D_2 in Ar (AlD)	1181.7 (1211.9 − 2 × 15.1)	1158 (1186.5 − 2 × 14.2)	23.7		
Cu; 10% H_2 in Ar (CuH)	1866.4 (1940.4 − 2 × 37.0)	1882 (1952.2 − 2 × 35.1)	−15.6		
		(1864)[c] (1933.4 − 2 × 34.7)	(2.4)[c]		
				1.387	1.388
Cu; 10% D_2 in Ar (CuD)	1346.1 (1384.3 − 2 × 19.1)	1356 (1391.6 − 2 × 17.8)	−9.9		(1.388)[c]
		(1343)[c] (1378.3 − 2 × 17.6)	(3.1)[c]		
Ni; 5% H_2 in Ar (NiH)	1920 (2000 − 2 × 40)	1906 (1976.6 − 2 × 35.3)	14		
				1.381	1.388
Ni; 5% D_2 in Ar (NiD)	1390 (1430 − 2 × 20)	1374 (1409.9 − 2 × 18.0)	16		

[a] From gas-phase electronic spectra; anharmonic term included $\nu_g = \omega_e - 2\omega_e x_e$. [b] Argon matrix at 14 K; IR spectra from this work; values in parentheses were calculated from eq 1-3 with $\rho_{\mathrm{AlH,D}} = 0.71998$, $\rho_{\mathrm{CuH,D}} = 0.71287$, and $\rho_{\mathrm{NiH,D}} = 0.71331$. [c] Matrix site effect at higher H_2 (D_2) concentration. [d] Reference 16.

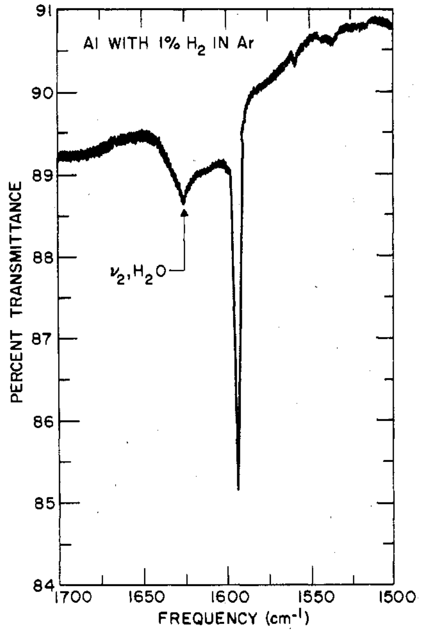

Figure 2. Infrared transmission spectrum of matrix-isolated (14 K) AlH produced in an aluminum hollow cathode with 1% H_2 in Ar as the discharge gas. Discharge operated for 45 min at 400 V, 45 mA with 10 mmol/h gas mixture flow rate and KCl deposition plate and windows.

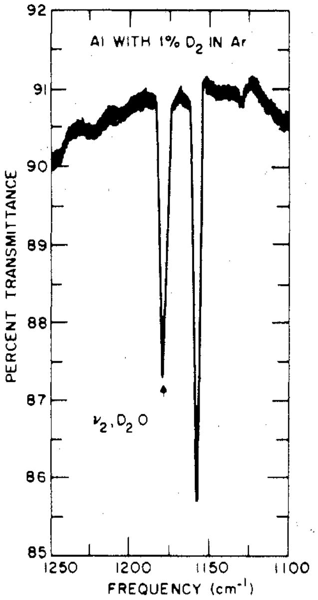

Figure 3. Infrared transmission spectrum of matrix-isolated (14 K) AlD produced in an aluminum hollow cathode with 1% D_2 in Ar as the discharge gas. Discharge operated 45 min at 400 V, 45 mA with 10 mmol/h gas mixture flow rate and KCl deposition plate and windows.

is 1.375 whereas our value as determined from the infrared data is 1.376. The first-order anharmonic correction term $\omega_e x_e$ and the harmonic frequency ω_e for the matrix-isolated molecules can be calculated using the formulas[12]

$$\begin{aligned} \nu_m{}^H &= \omega_e{}^H - 2\omega_e{}^H x_e{}^H \\ \nu_m{}^D &= \omega_e{}^D - 2\omega_e{}^D x_e{}^D \end{aligned} \tag{1}$$

where

$$\begin{aligned} \omega_e{}^D &= \rho\omega_e{}^H \\ \omega_e{}^D x_e{}^D &= \rho^2\omega_e{}^H x_e{}^H \end{aligned} \tag{2}$$

and

$$\rho = \left[\frac{m_M m_H/(m_M + m_H)}{m_M m_D/(m_M + m_D)}\right]^{1/2} \tag{3}$$

where m_M, m_H, and m_D are the masses of the metal (atomic weight), hydrogen, and deuterium, respectively. The values listed in Table I for ω_e and $\omega_e x_e$ for the aluminum hydride and deuteride are different from those of the gas phase owing to matrix perturbations. It is observed that for AlH and AlD (as well as CuH, CuD, NiH, and NiD) the anharmonic term $\omega_e x_e$ is slightly smaller in the matrix than in the gas phase, the major change occurring in the ω_e value.

When a Cu cathode is used, a doublet is observed when concentrations of H_2 (or D_2) greater than 5% in Ar are used. The bands appear at 1882 and 1864 cm^{-1} for H_2 and at 1356 and 1343 cm^{-1} for D_2 at concentrations greater than 5% H_2 or D_2 in Ar, but only the bands at 1882 and 1356 cm^{-1} (H_2 and D_2, respectively) appear at concentrations less than 5%. The extra bands appearing at the higher H_2 or D_2 concentrations probably arise from matrix site effects and their resulting perturbations. The peak splittings due to the reduced mass differences between the isotopes of Cu (and for Ni discussed below) are too small to resolve in our experiments. There is also the possibility that these additional bands are due to formation of higher hydrides; however, no other new bands were observed in the spectra which should arise (bending modes, asymmetric stretching modes, etc., depending on the polyatomic structure) if polyatomic molecules were forming. Any bands besides those for CuH (CuD) and the one additional band arising from the matrix site splitting all appeared regardless of the material used for the cathode and appeared also during the blank runs when the discharge was not operated. The previously reported gas-phase values, matrix shifts, and isotopic frequency ratios are listed in Table I. Comparison of these values again indicates that the bands observed in the infrared spectra are due to CuH or CuD molecules formed in the hollow-cathode sputtering source, subsequently matrix isolated and observed in the argon matrix by infrared spectroscopy.

The presently measured IR results for a Ni cathode with 1% H_2 (D_2) in Ar and previously reported values are listed in Table I. Recently, Nakata[13] has reported the infrared absorptions of hydrogen and deuterium chemisorbed on nickel which result in infrared bands at 1880 and 1360 cm^{-1}, respectively, close to the bands we observe but shifted (to lower frequency) by a greater extent than our bands when compared to the gas-phase values. We again conclude that NiH and NiD are the observed species.

Annealing of the matrices in the above experiments to 40 K did not appreciably alter the spectra in that no new bands appeared, although a general broadening and decreased absorbance were observed. Further evidence for the observation of the diatomic metal hydrides and deuterides is provided by the optical emission spectra obtained during operation of the hollow-cathode discharge. In all cases the molecular electronic emission spectrum due to the metal hydrides and deuterides was observed as well as atomic emission from excited argon and sputtered metal atoms. Assignments of these spectra are based on the published electronic spectra for the atomic and molecular species under discussion.[14-17] We were, however, unable to observe the electronic absorption spectra of the matrix-isolated metal hydrides and deuterides in the UV–visible spectral region. Presumably, the atomic absorption bands due to the matrix-isolated metal atoms swamp the metal hydride bands because the concentration of metal atoms greatly exceeds that of the diatomic molecular species. Furthermore, the oscillator strengths of the molecular spectral bands are much smaller than those for the metal atoms.

The question as to where the metal hydrides and deuterides are actually forming would appear, at least for these three metals, to have been answered by the direct observation, as discussed above, of the molecular emission spectra emanating from the bore of the hollow cathode during its operation. As an additional verification of this conclusion the hollow cathode and matrix deposition were operated in a "dual-flow" manner as discussed in section II. Operating the system in this manner prevents dissociation of H_2 or D_2 to H or D in the discharge followed by subsequent reaction. Under these conditions, the most likely reaction path would be between metal atoms and H_2 or D_2 molecules through either surface or bulk matrix diffusion. That this reaction mechanism, not surprisingly, is strongly excluded is evidenced by the fact that no metal hydride or deuteride infrared bands or electronic emission bands from the hollow cathode were observed when the system was operated in this manner. There is still the possibility that, under uniflow conditions, some of the atomic hydrogen or deuterium which is formed in the hollow-cathode discharge reacts with the sputtered metal atoms at the surface of the matrix where both species are still relatively mobile. This mechanism would be similar to that for the production of YbH and YbD by the simultaneous deposition of thermally generated atomic hydrogen or deuterium and ytterbium metal atoms in an argon matrix at 4 K.[11] Considering all the data, we favor the conclusion that the majority of the metal hydrides or deuterides are formed in the hollow-cathode discharge and subsequently isolated in the matrix.

In conclusion, we have observed the infrared absorption spectra in argon matrices of the diatomic hydrides and deuterides of Al, Cu, and Ni formed in a hollow-cathode sputtering source, a method which has proved quite convenient for this application. We have also been able, using this same technique, to obtain infrared spectra of the molecular hydride and deuteride species of Ti, V, Zr, Nb, Mo, and W. The resulting infrared spectra for the hydrides and deuterides of these metals formed in this manner are considerably more complicated than for the Al, Cu, and Ni compounds discussed above. The spectra were observed to change with the annealing of the matrix to 50 K, indicating that diatomic, higher polyatomic, and perhaps polymeric species are being formed and observed. At this time it can only be stated that hydride and deuteride molecular species of these metals are indeed formed, isolated, and observed by this technique; their exact structure and stoichiometry must, however, await further work.

Registry No. AlH, 13967-22-1; AlD, 22737-86-6; CuH, 13517-00-5; CuD, 13966-59-1; NiH, 14332-32-2; NiD, 14989-21-0.

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