atomic oxygen) under our experimental conditions. Arguments similar to those for H_2 chemisorption on the surface alloys may apply to O_2 chemisorption as well. The adsorption energy of $O_{2(a)}$ on Pt(111) is 8 kcal/mol.[39] This is apparently lowered by the presence of Sn adatoms in the surface alloys to the point that adsorption is not observed at 100 K. From this observation, the heat of adsorption of $O_{2(a)}$ on the alloy surfaces is at most about 5 kcal/mol; chemisorption of O_2 on the Sn/Pt(111) surface alloys has been weakened to an extent that $O_{2(a)}$ is essentially a physisorbed species. This decrease is due to an electronic effect, since we have observed molecular O_2 adsorption on Pt(111) surfaces covered with 0.25 and 0.33 ML of coadsorbed (unalloyed) Sn and Bi[52] on Pt(111); i.e., the ensemble required for adsorption of molecular O_2 should be present on the Sn/Pt(111) surface alloys. In addition, a similar electronic effect has been observed to decrease the heat of adsorption of ethylene on these Sn/Pt(111) surface alloys.[55] The origin of the barrier for O_2 dissociation on the alloys is more difficult to explain. A simple explanation is that decreasing the $O_{2(a)}$ well depth leads to a larger dissociation barrier. However, we have no information on the changes that occur in the $O_{(a)}$ potential well or on the changes that occur for the energy of the transition state itself. In addition to this type of electronic effect, the decomposition ensemble of Pt atoms required for O_2 dissociation may have been altered or removed by alloying Pt with Sn. Additional experiments and detailed theoretical work would be of benefit to an accurate explanation.

4.4. Comparison with Other Bimetallic Systems. For the UHV experiments described in this work, large structural changes of the Sn/Pt(111) surface alloys were not induced by small molecule chemisorption, as judged from LEED and AES measurements taken after exposure to the respective gases. This is in contrast to early AES measurements of Bouwman et al.[9] and later work by Hoflund et al.[16] using ISS, XPS, and scanning AES, on the chemisorption of H_2 and O_2 at the surfaces of polycrystalline Pt–Sn samples. The work of these authors demonstrated significant surface segregation effects into and laterally across the surface for specific adsorbates. A quantitative comparison of segregation on the polycrystalline Pt–Sn alloys and the ordered Sn/Pt(111) surface alloys is difficult, since the Sn/Pt(111) surfaces used in our work do not have a bulk distribution of Sn and this affects the thermodynamics and kinetics. However, the different observed behavior serves to highlight the attendant advantages of working with thin film alloys on single-crystal samples to produce specific bimetallic surfaces. The problem of surface segregation into and across (due to grain boundary effects) bulk alloy surfaces is mitigated to a large extent when thin surface alloys and/or overlayers on single-crystal substrates are utilized.

Metal overlayers are not without their own surface structural problems. For example, in a related study on the effects of the chemisorption of H_2, CO, and O_2 on Bi/Pt(111) interfaces,[52] small molecule adsorption was observed to induce island formation and structural changes in the overlayer at critical exposures. For the Bi/Pt(111) system, Bi atoms form chemisorbed overlayers with net repulsive Bi–Bi interactions and do not appear to alloy under experimental conditions.[52] Thus, the spatial positions of the Bi adatoms are not fixed as rigidly as the positions of the Sn atoms in the Sn/Pt(111) surface alloys. Surface adatom mobility, the global energetics of adsorption, surface reconstruction, and compound formation are strongly correlated effects which dictate the extent of surface segregation at bimetallic surfaces when exposed to chemisorbed species. All of these factors by necessity require the use of surface structural probes that independently address long-range order and surface adsorbate site geometry. In the case of the Sn/Pt(111) surface alloys, the ability to form a bimetallic surface with the second metallic component incorporated *in* the surface layer as opposed to *on* the surface has a dramatic effect on the chemistry of small molecule adsorbates. The differences between the two different types of bimetallic surfaces used in model studies of chemisorption and catalysis are highlighted in the study presented here.

Acknowledgment. Support from the Department of Energy through the Morgantown Energy Technology Center is gratefully acknowledged by M.T.P. B.E.K. acknowledges the support of this work by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division. We acknowledge Dr. Mark Jones for help with the TDMS simulation code and Dr. Walt Ellis for helpful discussions.

---

[55] Paffett, M. T.; Gebhard, S. C.; Windham, R. G.; Koel, B. E. *Surf. Sci.* 1989, *223*, 449.

Decomposition of an Organophosphonate Compound (Dimethyl Methylphosphonate) on the Ni(111) and Pd(111) Surfaces

X. Guo, J. Yoshinobu, and J. T. Yates, Jr.*

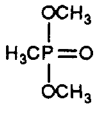
Surface Science Center, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

(Received: December 27, 1989)

The decomposition of a model organophosphonate compound, dimethyl methylphosphonate (DMMP), by Pd(111) and Ni(111) surfaces has been studied by using Auger spectroscopy (AES) and temperature-programmed reaction spectroscopy (TPRS). In both cases, in the absence of O_2, thermal decomposition of DMMP occurs [Pd, below 300 K; Ni, below 340 K] based on the observation of desorption-limited H_2 and CO evolution. Phosphorus is deposited on both Pd(111) and Ni(111) surfaces following the DMMP decomposition. Oxidation at 1075 K removes the surface phosphorus on Pd(111). On Ni(111), however, surface phosphorus cannot be removed by oxidation at 1075 K, nor is preoxidized Ni(111) active for phosphorus removal at 1075 K. By comparison with similar experiments on Mo(110), it appears that the early transition metals may be more suitable for the catalytic oxidation of organophosphonate compounds, on the basis of the lower temperature for sustained removal of surface phosphorus by oxygen on Mo(110) [900 K] compared to Pd(111) [1075 K].

Introduction

The surface chemistry of organophosphonate compounds has been the subject of a recent review[1] due to their relevance as environmentally hazardous materials. The sustained heterogeneous catalytic decomposition of the model compound, dimethyl methylphosphonate (DMMP), has been achieved under oxidizing



$$H_3C\overset{\displaystyle OCH_3}{\underset{\displaystyle OCH_3}{P}}{=}O$$

DMMP

---

[1] Ekerdt, J. G.; Klabunde, K. J.; Shapley, J. R.; White, J. M.; Yates, Jr., J. T. *J. Phys. Chem.* 1988, *92*, 6182.

0022-3654/90/2094-6839$02.50/0 © 1990 American Chemical Society

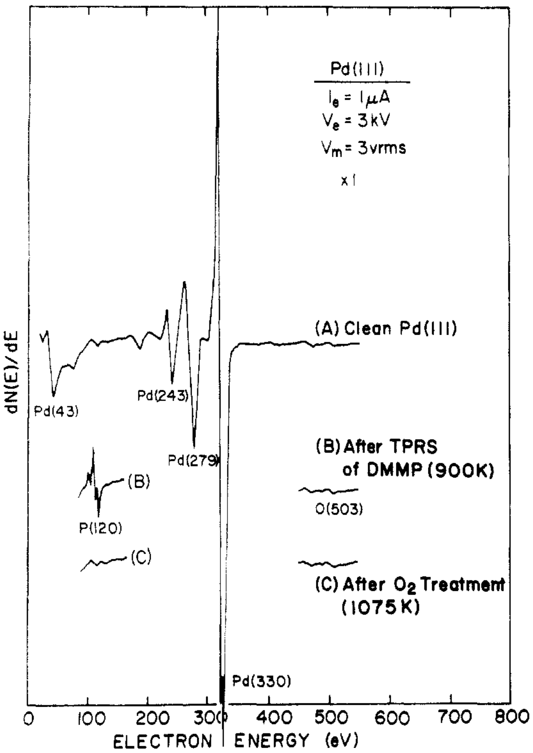


Figure 1. Auger electron spectra of the Pd(111) surface: (A) clean Pd(111) surface; (B) after temperature-programmed reaction of DMMP up to 900 K; (C) after oxygen treatment (5×10^{-8} Torr; 1 h) at 1075 K.

conditions in this laboratory on a Mo(110) surface.[2] This is the first and only report of the sustained heterogeneous catalytic decomposition of an organophosphonate compound, although other studies of the adsorption and decomposition of DMMP on transition metals are available.[1,16] In the present comparative study, Pd(111) and Ni(111) are investigated as model catalysts for the decomposition of DMMP, and the results are compared to earlier studies on Mo(110).

Both Pd ([Kr]$4d^{10}$) and Ni ([Ar]$3d^84s^2$) are late transition metals in group VIIIA (10) in the periodic table, whereas Mo ([Kr]$4d^55s$) in group VIA (6) is an early transition metal. In our comparison of the behavior of bcc-Mo(110) with fcc-Pd(111) and fcc-Ni(111), surface planes exposing the most dense surface packing of metal atoms have been selected in each case.

Experimental Section

The experiments were performed in an ultrahigh-vacuum chamber described in detail previously.[3] Briefly, it contains two collimated microcapillary array molecular beam dosers, a shielded and apertured quadrupole mass spectrometer (QMS) with differential pumping, an Auger electron spectrometer (AES), and other measurement techniques. Both the Ni(111) and Pd(111) crystals have been cleaned extensively and used for other experiments previously.[4,5] The DMMP (99.4%, Morton Thiokol) was further purified by five freeze–pump–thaw cycles with continuous pumping. The DMMP mass spectrometer fragmentation pattern for major ions was similar to that previously reported.[2]

Results and Discussion

DMMP Decomposition on Ni(111) and Pd(111): Surface Residues. The absence of stable chemisorbed species produced by DMMP decomposition on transition metals is crucial for achieving sustained DMMP catalytic decomposition, for it has been determined that on Mo(110)[2] and other surfaces[1] phosphorus and carbon can poison the catalyst, reducing or inhibiting the catalytic activity. This basic type of information has been obtained by Auger electron spectroscopy.

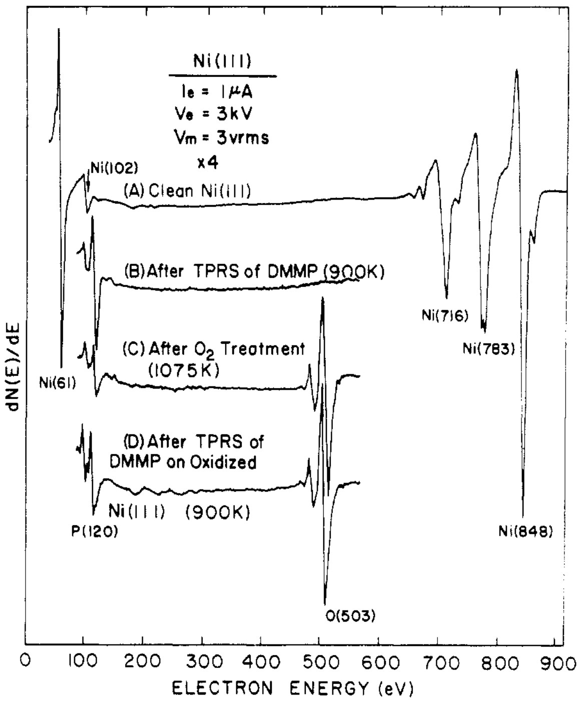


Figure 2. Auger electron spectra of the Ni(111) surface: (A) clean Ni(111) surface; (B) after temperature-programmed reaction of DMMP up to 900 K; (C) after oxygen treatment (5×10^{-8} Torr; 1 h) at 1075 K; (D) after temperature-programmed reaction of DMMP on preoxidized Ni(111).

The Auger electron spectrum of the clean Pd(111) surface is shown in Figure 1A. Also shown are spectra taken after temperature-programmed reaction spectroscopy (TPRS) of DMMP at $T < 900$ K (B) and after subsequent oxygen treatment of the surface at 1075 K with $\sim 5 \times 10^{-8}$ Torr of O_2 (C). It can be seen that phosphorus is left on the surface following DMMP decomposition. No oxygen is present following DMMP decomposition as indicated by the absence of the O(KLL) Auger peak at 503 eV. It is important to note that phosphorus left on Pd(111) can be removed by oxidation at high temperature. The oxygen treatment at 1075 K restores the Pd(111) surface to its clean condition as shown in Figure 1C. It should also be noted that a small amount of carbon was left on Pd(111) as determined by an O_2 adsorption/CO desorption experiment. In this case, Auger spectroscopy is insensitive to carbon because the C(KLL) Auger peak at 272 eV overlaps with the Pd(MNN) peak at 279 eV.

On Ni(111), DMMP decomposition yields similar results: neither carbon nor oxygen is left on the surface, but phosphorus remains following the TPRS of DMMP (compare Figure 2, parts A and B). In contrast to the behavior of Pd(111), oxygen treatment at 1075 K for about 1 h does not remove all surface phosphorus as shown by Figure 2C. The reduced P(LMM) Auger peak intensity at 120 eV may be due to nickel oxide formation following oxygen treatment.

A similar exploratory experiment was carried out with DMMP on an oxidized Ni(111) surface.[4] Figure 2D shows the Auger spectrum following the TPRS of DMMP ($T < 900$ K) on a preoxidized Ni(111) surface (initially free of phosphorus). Again, surface phosphorus appears after the reaction, indicating that the catalytic activity of the oxidized Ni(111) is similar to Al_2O_3[6] and Fe_2O_3.[7]

---

(2) Smentkowski, V. S.; Hagans, P.; Yates, Jr., J. T. *J. Phys. Chem.* **1988**, *92*, 6351. U.S. Patent No. 4,871,526.

(3) Gates, S. M.; Russell, Jr., J. N.; Yates, Jr., J. T. *Surf. Sci.* **1984**, *146*, 199.

(4) Guo, X.; Yoshinobu, J.; Yates, Jr., J. T. *J. Chem. Phys.* **1990**, *92*, 4320.

(5) Guo, X.; Hoffman, A.; Yates, Jr., J. T. *J. Phys. Chem.* **1989**, *93*, 4253.

(6) Templeton, M. K.; Weinberg, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 774.

(7) Henderson, M. A.; Jin, T.; White, J. M. *J. Phys. Chem.* **1986**, *90*, 4607.

(8) Hegde, R. I.; Greenlief, C. M.; White, J. M. *J. Phys. Chem.* **1985**, *89*, 2886.

(9) Gdowski, G. E.; Felter, T. E.; Stulen, R. H. *Surf. Sci.* **1987**, *181*, L147.

(10) Guo, X.; Hoffman, A.; Yates, Jr., J. T. *Surf. Sci.* **1988**, *203*, L672.

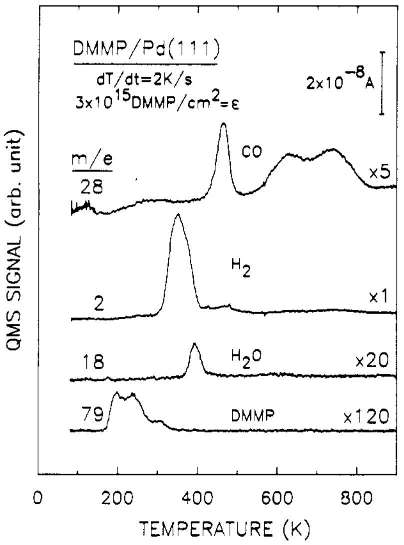
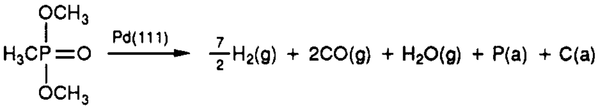


Figure 3. Temperature-programmed reaction spectra of DMMP on Pd(111). DMMP adsorption temperature = 87 K; DMMP exposure = ~3 × 10^{15} molecules/cm^2; heating rate = 2 K/s.

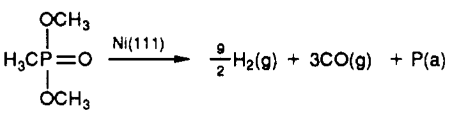
DMMP Decomposition on Pd(111) and Ni(111): Desorption Products. The temperature-programmed reaction spectra (TPRS) of DMMP on Pd(111) are shown in Figure 3. The adsorption temperature was 87 K; the exposure was about 3 × 10^{15} DMMP molecules/cm^2. Besides the molecular DMMP desorption below 350 K, other major desorption species observed are H_2 with maximum desorption rate at 350 K and major amounts of CO at 464, 630, and 736 K. A smaller desorption signal of H_2O was detected at 394 K. No desorption of CO_2 (44 amu), CH_4 (16 amu), or CH_3OH (32 amu) was observed, in contrast to measurements on Rh(100).[8] From this information, combined with the AES observation, the total decomposition reaction of DMMP on Pd(111) can be written as



$$\mathrm{H_3C\overset{OCH_3}{\underset{OCH_3}{P}}{=}O} \xrightarrow{\mathrm{Pd(111)}} \frac{7}{2}\mathrm{H_2(g)} + 2\mathrm{CO(g)} + \mathrm{H_2O(g)} + \mathrm{P(a)} + \mathrm{C(a)} \tag{1}$$

The H_2 desorption temperature is similar to that of H_2 from pure hydrogen adsorbed on Pd(111),[9,10] indicating that the C–H bond in DMMP may already break below ~300 K. The first CO desorption process (464 K) is similar to that of pure CO chemisorbed on Pd(111).[11] Therefore CO is probably evolved at this temperature via a desorption-limited process, implying that CO(a) is formed from DMMP decomposition below ~400 K. This further indicates that some P–OC bond scission occurs below 400 K. Since the first CO desorption process does not accompany CO_2 formation, it is likely that the P=O bond in some thermal degradation products of DMMP is stable above 464 K. The two high-temperature CO desorption processes (630 and 736 K) are not characteristic of pure CO desorption from Pd(111)[11] and may indicate the occurrence of the reactions C(a) + O(a) → CO(g), P–OC → P(a) + CO(g), or C–PO → P(a) + CO(g). Isotopic mixing experiments of the type performed for CH_3OH/Pd(111)[12] would differentiate the three processes.

Temperature-programmed reaction spectroscopy of DMMP on Ni(111) yields major amounts of H_2 with a maximum desorption rate at 377 K and CO (427 and 639 K), as shown in Figure 4. Thus the total reaction is



$$\mathrm{H_3C\overset{OCH_3}{\underset{OCH_3}{P}}{=}O} \xrightarrow{\mathrm{Ni(111)}} \frac{9}{2}\mathrm{H_2(g)} + 3\mathrm{CO(g)} + \mathrm{P(a)} \tag{2}$$

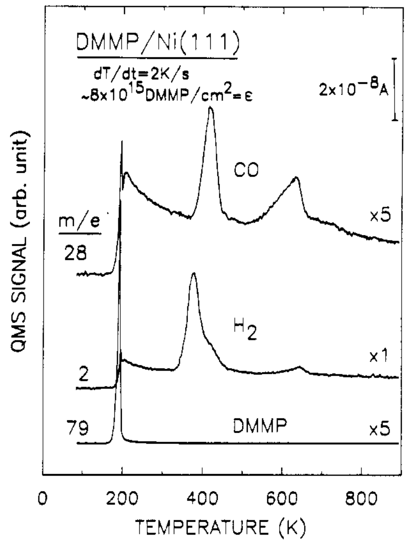


Figure 4. Temperature-programmed reaction spectra of DMMP on Ni(111). DMMP adsorption temperature = 87 K; DMMP exposure = ~8 × 10^{15} molecules/cm^2; heating rate = 2 K/s.

The H_2 desorption maximum at 377 K resembles that of pure H_2 on Ni(111),[13] indicating that C–H bond scission occurs below ~340 K. The CO desorption at 427 K also resembles that of CO on Ni(111),[14] indicating that the P–OC bond scission temperature is probably below ~370 K. The higher temperature CO desorption process corresponds to the temperature (~600 K) for the reaction C(a) + O(a) → CO(g), on Ni(111).[15] The temperature ~600 K therefore corresponds to the upper limit for the thermal stability of the P=O bond and the C–P bond in a thermal decomposition species derived from DMMP.

Also shown in Figure 4 is the DMMP multilayer desorption feature at 193 K from Ni(111), similar to that observed at ~197 K from Pd(111) (cf. the lowest temperature feature in Figure 3, which grows continuously with increasing DMMP exposure).

Continuous DMMP Decomposition under Oxidizing Conditions on Pd(111). Because of the demonstrated ability of oxygen to remove adsorbed phosphorus from Pd(111), the continuous catalytic decomposition of DMMP was studied only on Pd(111). These studies have been carried out for two DMMP + O_2 mixtures (1:2 and 1:10) at two surface temperatures (945 and 1075 K). The flux ratio of DMMP to O_2 effusing through the doser is 0.25 and 0.051 for these two mixtures.

The experiments were carried out in a similar manner to those on Mo(110),[2] i.e., the QMS monitors the scattered gas signals when the crystal intercepts the mixed flux of DMMP + O_2. For comparison, first at 1075 K we performed the experiment with a pure DMMP flux (~3 × 10^{14} molecules/(cm^2 s)). Following 180-s exposure to DMMP, the Auger spectrum of the surface showed a P(LMM) peak at 120 eV, confirming the DMMP decomposition. This experiment clearly shows that a fraction of the incident DMMP molecules can stick and decompose on Pd(111) even at a surface temperature as high as 1075 K.

Next, we did an experiment with a 1:10 DMMP + O_2 mixture (total flux ~3 × 10^{14} molecules/(cm^2 s)) at the same Pd(111) temperature, 1075 K. Following of 7000-s exposure, the Auger spectrum of the Pd(111) surface showed no P(LMM) peak, suggesting that *a sustained catalytic condition was reached in which there is no phosphorus deposition.* For continuous DMMP decomposition on Pd(111) the surface is free of a measurable coverage of O(a) following this experiment at 1075 K. At the surface temperature of 945 K, however, a similar experiment left

---

(11) Guo, X.; Yates, Jr., J. T. *J. Chem. Phys.* **1989**, *90*, 6761.

(12) Guo, X.; Hanley, L.; Yates, Jr., J. T. *J. Am. Chem. Soc.* **1989**, *111*, 4253.

(13) Russell, Jr., J. N.; Chorkendorff, I.; Lanzillotto, A.-M.; Alvey, M. D.; Yates, Jr., J. T. *J. Chem. Phys.* **1986**, *85*, 6186.

(14) Miller, J. B.; Siddiqui, H. R.; Gates, S. M.; Russell, Jr., J. N.; Yates, Jr., J. T.; Tully, J. C.; Cardillo, M. J. *J. Chem. Phys.* **1987**, *87*, 6725.

(15) Erley, W.; Wagner, H. *Surf. Sci.* **1978**, *74*, 333.

(16) Henderson, M. A.; White, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 6939.

a substantial coverage of phosphorus on the surface, as determined by the Auger spectrum.

The experiments with a 1:2 DMMP + O_2 mixture at 945 and 1075 K left phosphorus on the Pd(111) surface after 3600-s exposure.

These results therefore suggest that Pd(111) is an effective catalyst for the continuous decomposition of DMMP in excess O_2 at 1075 K. However, catalytic activity is not sustained at 945 K on Pd(111) at a DMMP:O_2 incident flux ratio of 0.051.

Comparison of Mo, Pd, and Ni for the Catalytic Decomposition of DMMP under Oxidizing Conditions. We have previously reported that a sustained catalytic decomposition of DMMP may be achieved on Mo(110) at 898 K using a flux ratio of 0.5 DMMP:O_2.[2] The present work indicates that Pd(111) exhibits sustained catalytic decomposition capability at a flux ratio of 0.051 DMMP:O_2 at 1075 K and that surface phosphorus does not deposit at this temperature. Under the same incident gas ratio conditions on Pd(111) at 945 K substantial phosphorus deposition occurs. Thus, somewhere between 945 and 1075 K surface phosphorus oxidation occurs at a rate sufficient to maintain the Pd(111) surface clean for DMMP decomposition. Ni(111) and preoxidized Ni(111) surfaces deposit phosphorus which cannot be removed by oxygen treatment at 1075 K.

We therefore have established the order of catalytic reaction activity among three transition metals for sustained catalytic decomposition of DMMP under oxidizing conditions, namely, Mo > Pd > Ni, based on the temperature needed to prevent phosphorus build up under continuous reaction conditions. In both cases where sustained catalytic decomposition is observed (Mo, Pd), it has been found that the removal of surface phosphorus by oxygen is the key to maintenance of a stable DMMP catalytic decomposition process over long periods of time.

Directions for Future Research. On the basis of the comparison between Mo (early transition metal), Pd, and Ni, it may be speculated that the early transition metals will be more useful than the late transition metals for the catalytic decomposition of organophosphorus compounds. Metals in group IVA (4) and VA (5) should be studied to determine whether lower temperatures for the catalytic decomposition of organophosphonates are possible compared to Mo. The key issue is probably the reduction of the activation energy for surface phosphorus oxidation by proper choice of the transition metal, and it is possible that this objective may be achieved by moving to the very early transition metals. In addition, specific promoters for phosphorus oxidation on transition metals should be sought.

Summary

The decomposition of DMMP has been studied on Ni(111) and Pd(111). The results are summarized as follows:

1. DMMP decomposes on Pd(111) into H_2(g), CO(g), and H_2O(g), leaving P(a) and a small amount of C(a) residues on the surface. Both residues can be removed by oxidation using O_2(g) at 1075 K.
2. On Ni(111), DMMP decomposes into H_2(g), and CO(g), leaving P(a) on the surface which cannot be removed by oxidation at 1075 K. P(a) is removed only by Ar^+ sputtering.
3. A sustained condition for continuous DMMP catalytic decomposition can be reached on Pd(111) with a 0.051 DMMP:O_2 flux ratio at a surface temperature of 1075 K. The removal of surface phosphorus by oxidation is the key process, and the DMMP oxidation reaction appears to occur on a Pd(111) surface that contains only small coverages of P(a), O(a), and C(a) under the conditions of this experiment.
4. These results, compared to earlier studies on Mo(110), suggest that the early transition metals are more active for catalytic decomposition of organophosphonate compounds under oxidizing conditions.

Acknowledgment. We gratefully acknowledge the support of this work by the Army Research Office under Contract No. DAAL 03-89-K-0005.

Registry No. DMMP, 756-79-6; Ni, 7440-02-0; Pd, 7440-05-3; P, 7723-14-0.

Studies of Surface Recombination Velocity at Cu/CdS(11$\bar{2}$0) Interfaces

Y. Rosenwaks,[†] L. Burstein,[†] Yoram Shapira,[†] and D. Huppert*[,‡]

Department of Electron Devices and Materials, Faculty of Engineering, and Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry, Tel Aviv University, Ramat Aviv 69978, Israel

(Received: January 2, 1990; In Final Form: April 13, 1990)

Direct measurement of the surface recombination velocity (SRV) on etched CdS(11$\bar{2}$0) and at its interface with Cu (deposited by aqueous $CuSO_4$ solutions and in situ thermal evaporation) was achieved by using ultrafast time-resolved photoluminescence. Correlation with interfacial composition and chemistry was based on Auger electron spectroscopy (AES) and atomic absorption spectroscopy. The surface electronic structure was studied by using surface photovoltage spectroscopy. The results show that the original CdS SRV increases sharply as a function of Cu coverage. The SRV stabilizes around 1×10^6 cm/s (3 orders of magnitude above the clean surface value) at Cu coverage of about 1 monolayer, as estimated from AES results on in situ deposited Cu/CdS. The results are explained in terms of Cu–S compound-derived recombination centers at the Cu/CdS interface. The results are compared with thermally evaporated Cu/CdS interfaces, where a similar Cu coverage dependence and SRV mechanism are apparent.

Introduction

It is widely accepted that surface recombination of carriers at semiconductor surfaces severely limits the performance of minority-carrier devices such as solar cells, detectors, and bipolar transistors. Surface recombination velocity (SRV) is a good means of parametrizing such a surface property. For example, it was recently demonstrated[1,2] that an improvement in the SRV value of GaAs by 2 orders of magnitudes had led to a 60-fold improvement in the gain of a heterojunction bipolar transistor.

To date, little has been done regarding research, investigation, or characterization of the factors affecting the SRV. Most of the works are limited to evaluation of SRV on thin film surfaces as

---

[†] Faculty of Engineering.

[‡] School of Chemistry.

(1) Nottenburg, R. N.; Sandroff, C. J. S.; Humphrey, D. A.; Hollenbeck, T. H.; Bhat, R. *Appl. Phys. Lett.* **1988**, *52*, 218.

(2) Sandroff, C. J.; Nottenburg, R. N.; Bischoff, J. C.; Bhat, R. *Appl. Phys. Lett.* **1987**, *51*, 33.