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OPTICAL PROPERTIES AND SURFACE MORPHOLOGY STUDIES OF

PALLADIUM CONTACTS ON MERCURIC IODIDE SINGLE CRYSTALS

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ABSTRACT

Palladium is chemically suitable for electric contacts on mercuric iodide detectors for photon and nuclear radiation detection, so the understanding of palladium contacts is important for fundamental and practical scientific purposes. A study has been conducted on the surface morphology of evaporated contacts using Atomic Force Microscopy (AFM) and optical transmission and reflection. Evaporated palladium coatings are typically nonuniform and may deposit selectively on mercuric iodide surface defects. Reflection measurements show that coating thickness and the surface treatment affect the intensity, position and shape of a reflected peak characteristic of the mercuric iodide structure. The results indicate that the band gap energy in the surface of the mercuric iodide is lowered by palladium contacts.

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I. INTRODUCTION

Palladium is an electrode material which is used in mercuric iodide photonic devices (1). The nature of the electrode/substrate zone can be important in applications ranging from gamma rays to visible light. The physical properties of palladium contacts have been studied extensively by low temperature photoluminescence (2) and thermally stimulated conductivity (TSC) (3). These techniques, and the usual process of vacuum deposition of the contacts, require exposing the samples to vacuum conditions. Recently, it has been shown that a dynamic vacuum contributes to the formation of defects on mercuric iodide surfaces (4) and affects surface leakage currents (5). It would be useful to distinguish between surface alterations due to the evacuation and deposition process, and those due to post deposition by interaction between palladium and the mercuric iodide substrate.

This paper presents a study of the surface morphology of semitransparent palladium contacts on mercuric iodide crystals using atomic force microscopy (AFM) and scanning tunneling microscopy (STM). Optical transmittance and reflectance properties of the contacts are also reported and reveal complementary information about the contact/ mercuric iodide interface. All of the characterization techniques were performed in ambient conditions. These results may lead to techniques of device fabrication where defects due to applying electrodes are minimized.

II. EXPERIMENTAL

The palladium contacts were vacuum evaporated resistively onto mercuric iodide slices which have been sectioned from single crystals by string sawing and polishing in potassium

iodide solution at EG&G/EM Santa Barbara Operations. Increased evaporation times were applied to achieve increased coating thicknesses.

The reflectance measurements were performed with the set-up shown in figure 1, using a 4 mm diameter, collimated white light beam from a quartz-halogen lamp. The beam reflected from the sample surface was collected and transmitted by an optical fiber to a SPEX 1877D Triplemate spectrometer equipped with a liquid nitrogen cooled, charge coupled device (CCD), a grating with 300 grooves/mm and a 30 μm slit.

A Digital Instruments Nanoscope II was employed for the AFM and STM studies. It is equipped with a piezoelectric tube scanner having an effective range from about 0.5 to 12 μm , and it was calibrated using a gold grid and mica standards. The cantilevers for the AFM are gold coated silicon nitride, with a force constant of 0.06 N/m, and a feedback voltage of -2.0 V was used for the AFM scans. The STM uses platinum-iridium tips, and the setpoint current was maintained at 1.0 nA, with a 300.0 mV tunneling voltage and a usual scan rate of 1 Hz. Measurements of surface features and image processing were performed using the software available with the Nanoscope II system.

III. RESULTS AND DISCUSSION

The transmission of white light was measured for coated mercuric iodide slices which have been coated with palladium. Sample S1 was uncoated. Samples S2, S3, S4, and S5 were a set with progressively thicker palladium coatings, and S5 had the standard coating for gamma ray detectors prepared at EG&G/EM. Taking the transmission of S1 as 100%, the transmissions were normalized to 97%, 77% and 42% and approximately 10% for S2, S3, S4

and S5, respectively. Nominal thicknesses for the thinner coatings were obtained using a previous calibration of the evaporation apparatus using the transmission through coated glass slides, and gave approximately 10 Å for S2, 50 Å for S3 and 85 Å for S4. The thickness for S% was approximately 1 µm and was measured by AFM. As expected, the transmission increases as the film thickness decreases.

The surface morphologies of S1 through S4 were examined by means of the AFM and are shown in figures 2(a) through 2(d), respectively. The mean-square surface roughnesses were measured in the usual way and are listed in table 1. Figure 2(a) shows a surface mechanochemically polished at Fisk University and aged at ambient for several weeks. An aged surface is expected to be rougher than an as-cleaved or freshly etched surface, due to the tendency of mercuric iodide to evaporate and to react with the ambient (6). The images of the progressively thicker palladium films in figures 2(b), 2(c) and 2(d) indicate that the coatings have large nonuniformities and discontinuities, even when the average thickness is many monolayers. During the evaporation preceding the deposition, or as a result of the deposition of a thin coating as in figure 2(b), the surface roughens, but as the coating thickens as in figure 2(d), the surface returns to the general range of the precoating roughness, as indicated in table 1. This behavior suggests that the initial nucleation of palladium overlayers may be at selected sites, which could be defects in the mercuric iodide surface.

The optical reflection spectra of the four samples were measured in the range 540-590 nm, which contains the broad peak centered around 558 nm that has been attributed (7) to exciton formation in α -mercuric iodide. The spectra have been curve fitted and are shown in figure 3(a). It is apparent that the peak broadens and shifts toward longer energy as the

thickness increases, S1 to S4. A peak shape parameter can be defined by I/FWHM , where I is the peak intensity above background, and FWHM is the peak width at half the maximum intensity. The peak position and the shape parameter, which has been normalized to 1.0 for the sharpest peak (S1), are shown as a function of transmission in figure 3(b). Both the position and the shape depend in a nominally linear way on the coating thickness, and the differences between the coated and the uncoated (S1) samples are significant. The reduction in the peak intensity in figure 3(a) as the coating thickens is expected, since the peak pertains to mercuric iodide, which is progressively obscured as the coating builds up unevenly on the surface. However, the reason for the broadening of the peak is not clear. An effect similar to this peak broadening was observed in GaAs (8).

It is quite significant that the peak position shifts as the coating thickens. The mercuric iodide responsible for this peak must consist of regions which are uncovered by coating, but might also include other regions where the coating is thin enough. It appears that the fundamental excitonic processes, which govern the light reflected from the uncoated or lightly coated regions are progressively affected by the increasing buildup of palladium. This peak shifting (7) indicates that the bandgap in the near-surface mercuric iodide is being reduced. The reduction for thickest coating, S4, is about 0.04 eV. This result suggests that palladium is doping the mercuric iodide and may be spreading to the uncoated regions by surface diffusion. There is other evidence, from photoluminescence measurements (2), that palladium coatings affect the non-stoichiometry of the interface.

The nature of the surface roughening during and after the Pd coating processes is shown in three dimensional presentation in figure 4. Figure 4(a) shows a freshly cleaved

surface; figure 4(b) shows a polished, etched in KI and aged surface; figure 4(c) shows a surface such as figure 4(b), but after evaporative palladium coating. The roughness parameters are 1.3, 9.9 and 27.9 nm from table 1, respectively. These results indicate again that the coating is not uniform and suggest that either the palladium preferentially builds up on selected defect sites, rather than uniformly, or else the coating uniformly deposits onto a surface which has been roughened by the evaporation process just preceding the deposition.

The surface of the palladium coating itself was investigated further. Some AFM results are shown in figure 5(a) and 5(b) for two magnifications. Figure 5(c) shows an STM image of an area similar to figure 5(b). These images show polycrystalline palladium, with a crystallite size of approximately 5 nm.

Figure 6 presents an optical micrograph of S5, which has the coating thickness which is typical of gamma ray detectors. The palladium surface (left side) shows areas which appear smooth, regions with sets of ripples, and depressions with widths of the order of 0.1 mm. A feature of special interest is the circular trace which is bisected by the coating, but whose outline still shows on the surface of the coating. This evidence shows that substrate topography is replicated to some degree on the surface of palladium coatings which are as thick as 1 μm . The detailed topography of palladium coatings and its relevance to detector performance will be examined in a forthcoming study.

CONCLUSIONS

Atomic Force Microscopy can be used to study palladium coatings deposited as electrodes on α -mercuric iodide by evaporation. These coatings are typically discontinuous

and nonuniform during the early stages of coating buildup, and at the full thickness of 1 μm the coating surface still shows evidence of the topography of the substrate. Reflectivity measurements of coated surfaces indicate that palladium contacting appears to alter the underlying mercuric iodide such that the energy band gap is reduced by the order of few tens of meV.

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Table 1 : Average surface roughnesses, R_a , as obtained by Atomic Force Microscopy.

Figure 2, R_a (nm)	Figure 4, R_a (nm)
(a) 4.0 ± 0.6	(a) 1.3 ± 0.3
(b) 6.0 ± 1.3	(b) 9.9 ± 2.2
(c) 4.3 ± 0.7	(c) 6.1 ± 1.3
(d) 4.2 ± 0.9	

FIGURES CAPTIONS

Figure 1: Schematic illustration of the reflection measurements set-up.

Figure 2: Atomic Force Microscope (AFM) images : (a) polished and aged mercuric iodide surface; (b) mercuric iodide surface with thin palladium coating; (c) thicker coating than (b); (d) thicker coating than (c).

Figure 3: (a) Curve fitted optical reflection spectra on samples S1, S2, S3 and S4 from figures 2(a), (b), (c) and (d), respectively : (b) The reflection peak position (curve a) and peak shape (curve b) versus the transmission.

Figure 4: Three dimensional AFM images of (a) cleaved mercuric iodide surface, (b) vacuum exposed mercuric iodide surface and (c) thin palladium film deposited on a surface such as shown in (b).

Figure 5: Images of palladium contacts : (a) AFM image of the grain structure, (b) magnified AFM image of grain structure, (c) STM image of similar area as (b).

Figure 6: Optical micrograph of sample S5, which has the coating typical for gamma ray detectors.

(a)

(b)

(c)

(d)

(a)

(b)

(c)

(a)

(b)

(c)

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