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Forming a p-n Heterojunction on GaP Photocathodes for H_2 Production Providing an Open-Circuit Voltage of 710 mV

Mauro Malizia, Brian Seger, Ib Chorkendorff, and Peter C. K. Vesborg*

CINF, Department of Physics, Technical University of Denmark, DTU

Building 311, Fysikvej, DK-2800 Kgs. Lyngby, Denmark

E-mail: peter.vesborg@fysik.dtu.dk

Electronic Supplementary Information

UV-Vis Spectroscopy

The absorption spectra for TiO_2 and Nb_2O_5 films are shown in Figure S1. A considerably high absorption in the visible light region is observed for the Nb_2O_5 film. This is most likely due to the presence of Nb in metallic phase, not completely oxidized during the deposition. For TiO_2 and Nb_2O_5 the bandgaps are found to be 3.1 eV and 3.5 eV, respectively, as depicted in the inset of Figure S1.

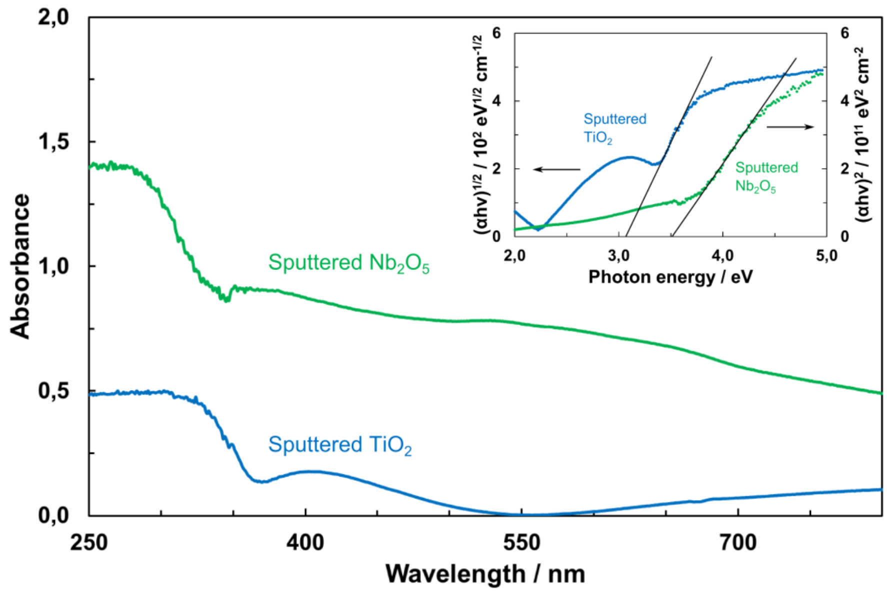

Figure S1: Absorption spectra for TiO_2 and Nb_2O_5 sputtered on quartz glass. Inset: Tauc plot for TiO_2 and Nb_2O_5.

X-ray Diffraction

The XRD data of both the TiO_2 and Nb_2O_5 films is shown in Figure S2. The peaks of the TiO_2 at 25.5°, 38.6°, 56.2°, and 63.8° correspond to anatase. The peak at 32° and 52°, and 67° are undefined peaks, but may be related to the underlying Si support. The extremely broad peaks of the Nb_2O_5 sample give little useful information. However without clear sharp peaks, it is evident that the Nb_2O_5 has, at most, a minimal degree of crystallinity.

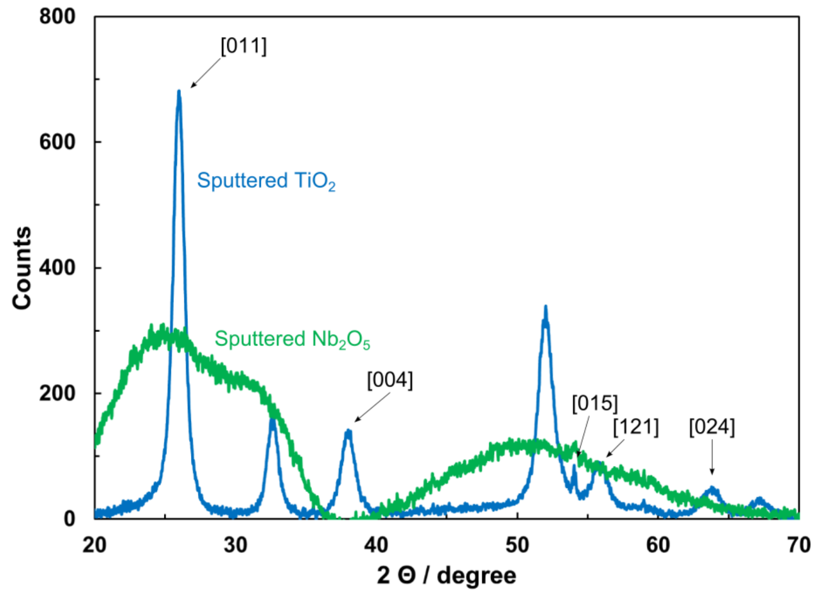

Figure S2: Cu Kα XRD peaks of TiO_2 and Nb_2O_5 sputtered on Si substrate showing the anatase structure of TiO_2 and the amorphous phase of Nb_2O_5.

Electrochemical Impedance Spectroscopy

The positioning of flat band potential of GaP, TiO_2 and Nb_2O_5 was determined by electrochemical impedance spectroscopy (EIS) using the Mott-Schottky relationship[1] expressed in the following Equation

$$\frac{1}{C^{-2}} = \frac{2}{e\varepsilon_r\varepsilon_0 A^2 N}\left(E - E_{FB} - \frac{k_B T}{e}\right) \quad (1)$$

where C is the space-charge region capacitance, e is the electronic charge, ε_r is the relative permittivity, ε_0 is the vacuum permittivity, A is the electrode surface area, N is the number of donors or acceptors, E is the applied voltage, E_{FB} is the flat band potential, k_B is Boltzmann's constant, and T is the temperature. Some assumption are made in the derivation of the Mott-Schottky equation, thus a standard nonlinear relationship between C^{-2} and E may not be observed if such assumptions are not fulfilled (*i.e.* space-charge region capacitance << Helmholtz layer capacitance, absence of surface states, frequency-independence of the dielectric constant ε_r, homogeneous spatial distribution of donors/acceptors, flat surface).[1,2]

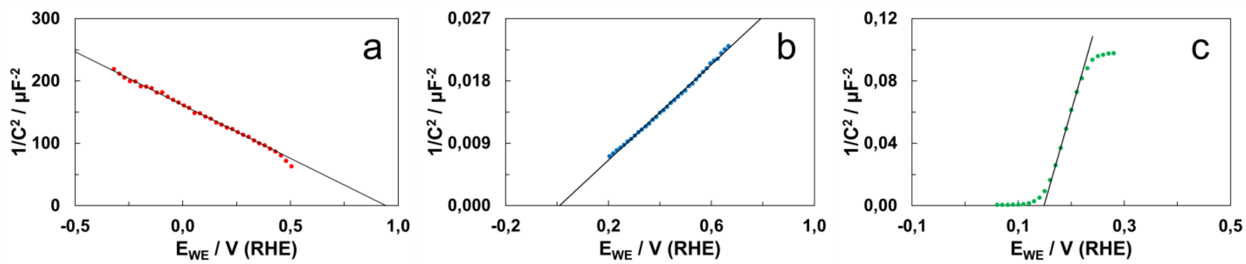

Figure S3: Mott-Schottky plot for (a) p-GaP, (b) n-TiO_2 and (c) n-Nb_2O_5 on Si substrate, measured using a modulation frequency of 1 kHz in 1 M $HClO_4$ in dark conditions.

The Mott-Schottky plot for p-GaP is shown in Figure S3a. By using Equation 1 and ε_r=11.1,[3] the flat band potential was found to be E_{FB}=0.92 V_{RHE} and the acceptors concentration was found to be $N_A=5.6\cdot10^{17}$ cm^{-3}. Mott-Schottky plots of the sputtered TiO_2 and Nb_2O_5 films deposited on Si are shown in Figures S3b and S3c. For TiO_2, ε_r is 75,[4] while E_{FB} was calculated to be -0.02 V_{RHE}. N_D is dependent upon the surface area, and SEM images have shown that the sputtered TiO_2 is quite rough.[5] If only the geometric area is taken into consideration, N_D would be $5\cdot10^{20}$ cm^{-3}. However, it should be noted that using a surface roughness of 3.2 or 10 would correspond to an N_D

of $5\cdot10^{19}$ cm^{-3} or $5\cdot10^{18}$ cm^{-3}, respectively. Determining the exact surface roughness and the effect of surface roughness on the Mott-Schottky impedance data is beyond the scope of this work. However, we can reasonably estimate that the actual donor density will be somewhere between $5\cdot10^{18}$ cm^{-3} and $5\cdot10^{20}$.

For Nb_2O_5 (ε_r=42),[5] E_{FB} was calculated to be 0.12 V_{RHE}. Again, the rough surface of the sputtered Nb_2O_5 made determining an effective surface area difficult. Using the same approach of TiO_2, we could estimate the N_D of Nb_2O_5 to be somewhere between $4\cdot10^{20}$ cm^{-3} and $4\cdot10^{18}$ cm^{-3}. Both metal oxides are n-type and characterized by a high donor density. The high donor density often introduces error for the determination of E_{FB} and carrier concentration due to the magnitude of the capacitance of the Helmholtz layer. Therefore, this can result in nonlinearity of the Mott-Schottky plot.[6]

We found an apparent E_{FB} for Nb_2O_5 that is more positive than the one of TiO_2, although the majority of studies on Nb_2O_5 place the value more negative than the one of TiO_2.[7]

The carrier density found in our Nb_2O_5 film is comparable to the carrier density reported for similar amorphous thin films, which indicates a highly disordered structure and probably a considerable presence of defects.[8]

References

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