Using Physical Vapor Deposition to Create Vanadium Dioxide for Security Printing and Anti-Counterfeiting

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Abstract

Vanadium Oxides are compounds that go through reversible metal-to-semiconductor transitions [Figure 1]. Vanadium Dioxide (VO_2) is the most commonly studied Vanadium Oxide because it has the lowest transition temperature at around 68ºC. Above the transition temperature VO_2 behaves as a metal and below the transition temperature VO_2 behaves as a semiconductor. In this work VO_2 will be made by Physical Vapor Deposition (PVD) [Figure 2]. PVD is a process that uses a target (Vanadium) and a carrier gas (Argon) to apply a thin metallic coating to a substrate (doped Silicon wafers). This exact process has not been used to make VO_2 before. Tests have to be performed on each sample to confirm that VO_2 was coated on the substrate and not another form of a Vanadium Oxide.

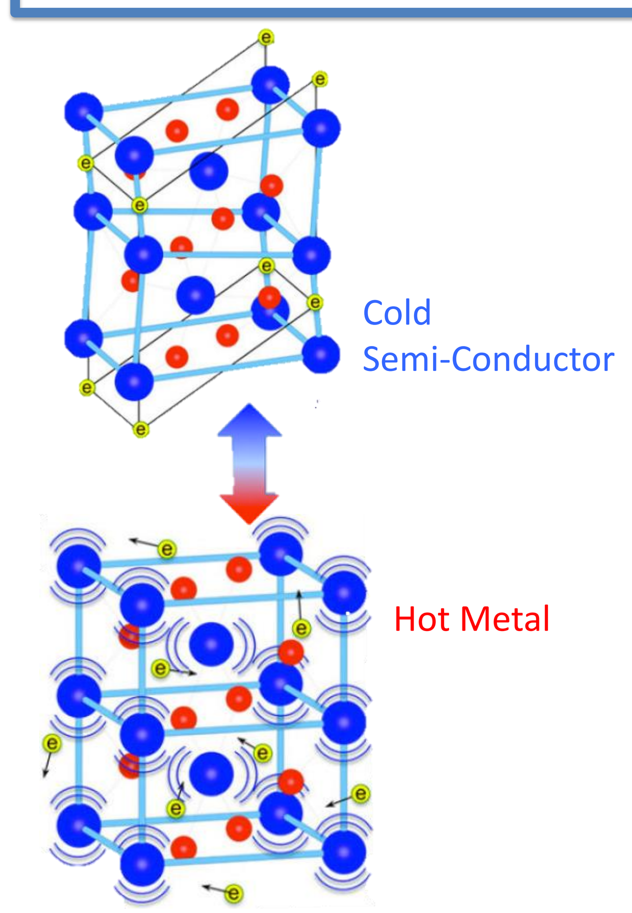

Figure 1: Metal-to-semiconductor phase transition
Photo from: Science Daily

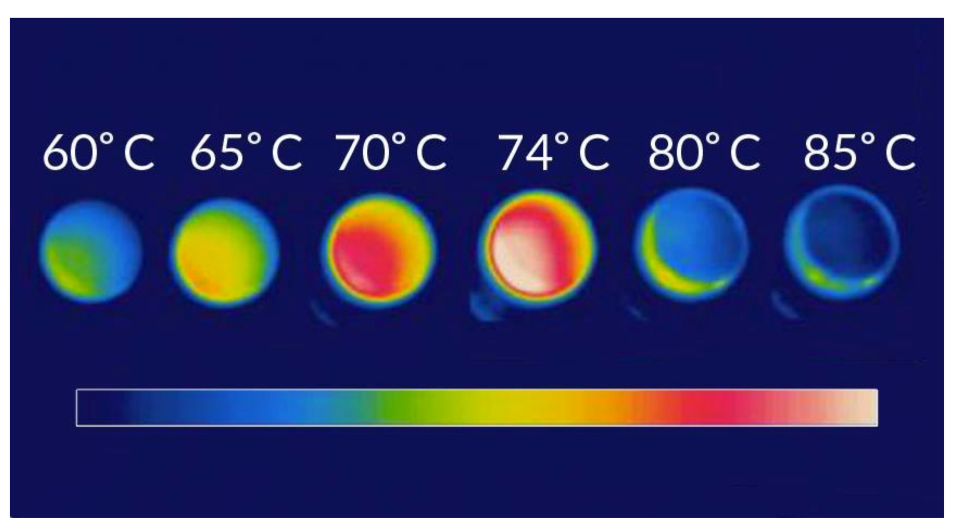

Figure 3: The IR properties of VO_2 at different temperatures
Photo from: Science News

Background Information

It is possible to use the metal-to-semiconductor transition properties of VO_2 to make antennas that change wavelength at the transition temperature. This could be used to detect when an undesirable temperature is reached such as food getting too warm and going bad. VO_2 can be used as an Infrared (IR) coating material for upconverting nanocrystals because of its changing IR properties [Figure 3]. The VO_2 is used on top of a QR code and can be used to help track and trace products for supply chain management.

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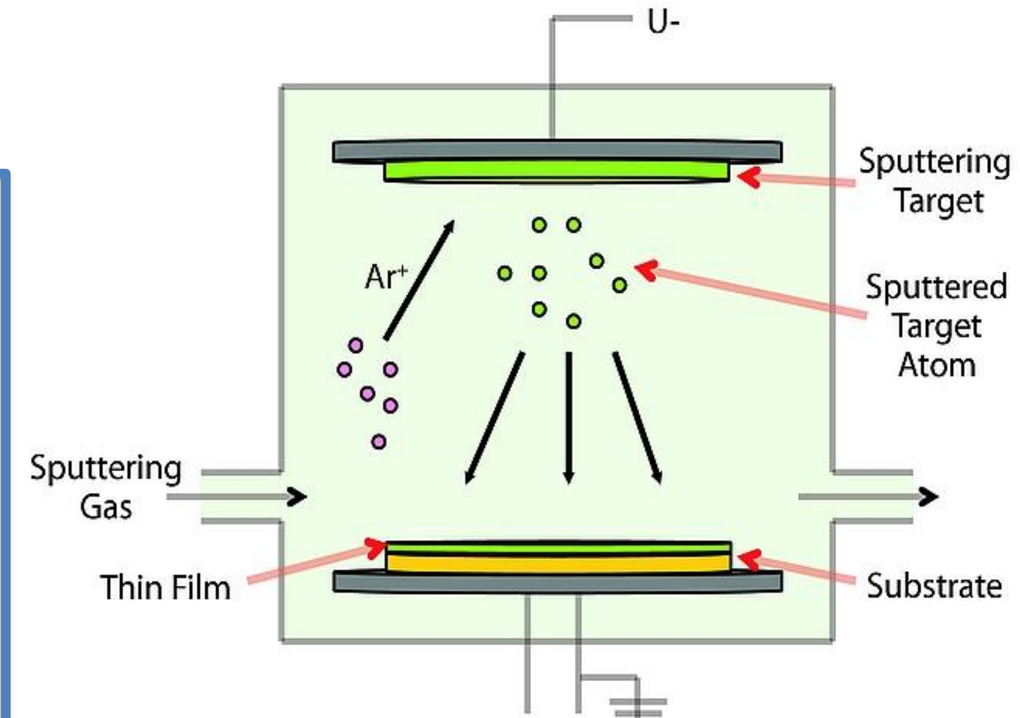

Figure 2: How PVD works
Picture from: Sigma-Aldrich

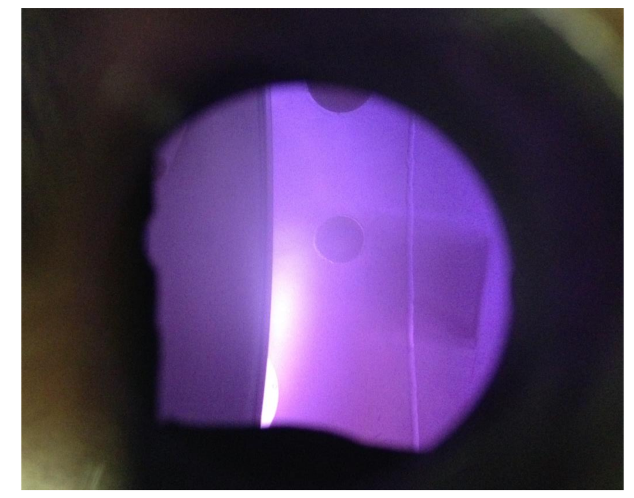

Figure 5: Plasma from the sputtering

Procedure

Making the VO_2:

- ❖ Clean off all of the substrates (doped Silicon wafer) [Figure 4a]
- ❖ Pump down the bell jar of the PVD machine to $1X10^{-5}$ Torr
- ❖ Move the substrates in front of the target (Vanadium)
- ❖ Turn on the bias (DC) to the target, set the flow rate and open the valves for the sputtering gas (Argon) and any other gas being used (Oxygen).
- ❖ Start the coating process [Figure 5]
- ❖ Move the substrates out of the way of the target [Figure 4b]
- ❖ Turn off bias and close gas valves
- ❖ Let the system cool down
- ❖ To change the crystal structure from amorphous to crystalline a heat treatment must be applied to the coating. For the heat treatment the sample was placed in a furnace and was heated at 500ºC for an hour [Figure 4c]

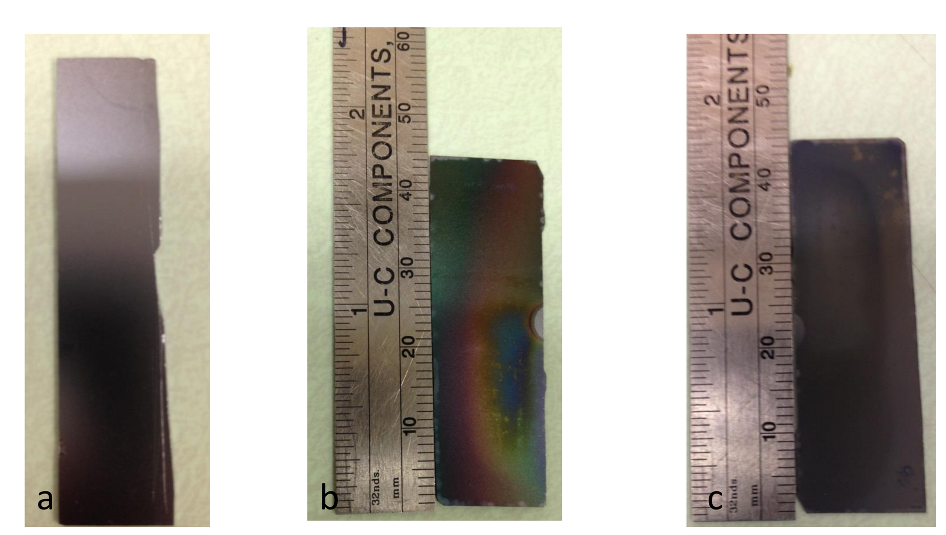

Figure 4: Silicon substrate with different coatings
a) untreated b) VO_2 coating c) after being heat treated

Characterization:

- ❖ Adhesion test [Figure 6]
- ❖ X-Ray Diffraction (XRD)
- ❖ Scanning Electron Microscopy (SEM)[Figure 7]/Energy Dispersive Spectroscopy (EDS)
- ❖ Four-point probe electrical conductivity
- ❖ Electron Backscatter Diffraction (EBSD)

Results

The first Vanadium Oxide on a Silicon wafer sample was made by PVD. But the SEM/EDS analysis of the film indicated that VO_2 was probably not formed. A vanadium bond layer was used to help with adhesion to the non-conductive wafer and there was a thin coating of Vanadium Oxide. Unfortunately the layer was too thin to give an accurate stoichiometric value.

The next Vanadium Oxide coating was done on a conductive Silicon wafer doped with Arsenic. Compared to the previous test, the Oxygen flow rate was increased from 2.3 sccm (standard cubic centimeters per minute) to 3.6 sccm. When SEM/EDS was used to determine the sample stoichiometry, there was double, by Atomic %, the amount of Oxygen on the coating than there was Vanadium [Figure 8]. XRD was performed and the results indicated that the film was either too thin or the coating was amorphous. Another sample was heat treated, XRD was performed and the results were again inconclusive meaning that the coating layer was probably too thin.

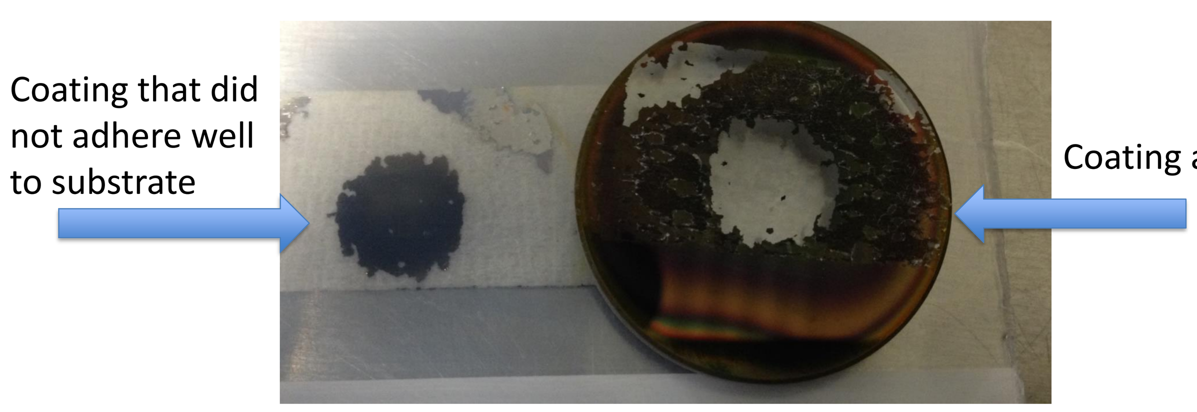

Figure 6: Results from tape peel adhesion test

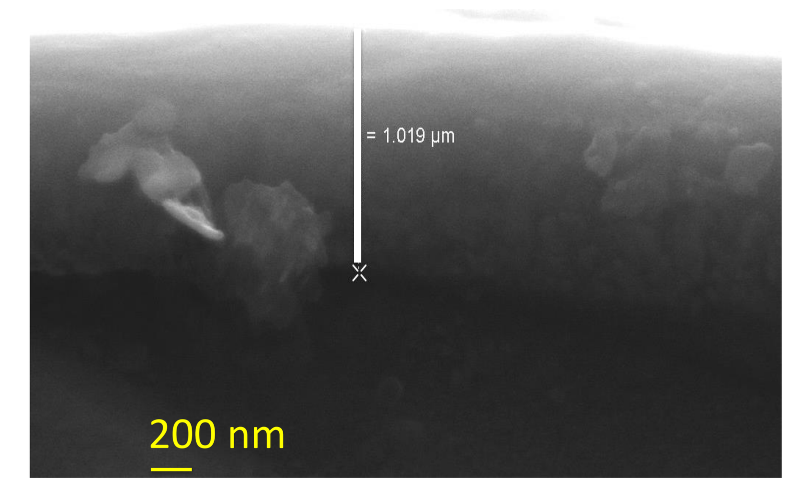

Figure 7: Light area is the VO_2 layer (about 1µm thick), the dark area is the doped Silicon wafer.

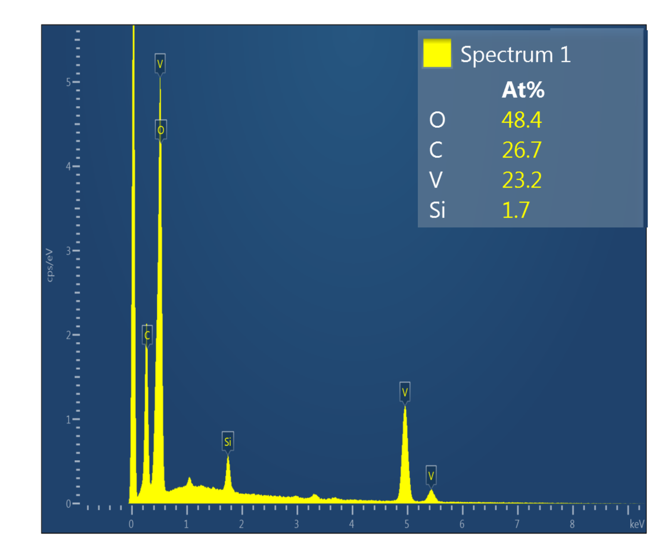

Figure 8: Showing the approximate stoichiometry of the coating by Atomic %

Conclusions & Future Work

Conclusions:

- ❖ PVD was used to make VO_2 according to stoichiometry
- ❖ The crystallinity of the coating has yet to be confirmed

Future Work:

- ❖ Measure electrical conductivity as a function of temperature
- ❖ Measure IR transmission
- ❖ Determine phase transition temperature