Supporting Information:

Chemical Solution Deposition of Epitaxial Carbide Films

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Experimental Details:

Source materials used to prepare the solutions are hexafluorotitanic acid (H_2TiF_6) (Aldrich 99.9%; 60 wt% in water), vanadyl sulfate hydrate (Acros), tantalum chloride (Aldrich), polyethyleneimine (PEI) (purchased from BASF Corporation of Clifton, NJ, without further purification), ethylenediaminetetraacidic (EDTA) (Aldrich 99.995%), ammonium hydroxide (Fisher Scientific, Trace Metal Grade), and 20% HF solution (Fisher Scientific, Trace Metal Grade). The water was purified to 18 MΩ.cm using a Milli-Q water treatment system.

The precursor solution to grow TiC films was prepared by binding titanium to PEI. The solution was made by adding H_2TiF_6 to PEI solution and water. The vanadium precursor solution was prepared by binding vanadium EDTA complex to PEI. In other words, the solution was made by adding vanadyl sulfate hydrate to water, followed by EDTA. The tantalum fluoride precursor was prepared by dissolving tantalum chloride in water. Tantalum hydroxide ($Ta(OH)_5$) precipitated out from this solution by adding an excess volume of ammonium hydroxide. These precipitates were rinsed with abundant deionized water to remove the chloride. The precipitates were then dissolved in 20% HF solution to form a TaF complex. PEI was then added to this TaF complex solution. Finally, ultrafiltrations were carried out to the above solutions using Amicon stirred cells and 3,000 molecular weight cut-off ultra filtration membrane under 60 psi argon pressure. The concentrations of Ti, V, and Ta were analyzed by a Horiba Jobin Yvon Ultima II inductively coupled plasma-atomic emission spectrometer (ICP-AES).

The film preparation:

Ti, V, or Ta precursor solution was spin-coated on sapphire substrates at 3000 rpm for 20 s. The precursor films were then heated to 650 ^oC at a ramping-up rate of 10 ^oC/min in a mixture gas of ethylene (10 sccm) and forming gas (10 sccm) and maintained at 650 ^oC for 2 h. The mixture gas was then switched off and the Ar gas (10 sccm) was turned on. The temperature was ramped up to 1000 ^oC in one hour, and the samples were annealed at 1000 ^oC for 3 h. Finally, the temperature of the furnace was cooled down to room temperature by turning off the power supply to the furnace.

The thickness of films is about 40 nm for one spin-coat. Thicker film could be deposited by increasing the concentration of metal ions and/or multiple spin-coats.

Characterization:

Ti, V, and Ta concentrations in precursor solutions were determined by a Horiba Jobin Yvon Ultima II inductively coupled plasma-atomic emission spectrometer (ICP-AES). X-ray diffraction (XRD) was used to characterize the crystallographic orientation of the films. The surface morphology and the surface roughness of the films were analyzed by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The microstructure of the films was further analyzed by transmission electron microscopy (TEM). The conductivities were measured from 5 K to 300 K under zero magnetic field using a standard four-probe technique by a Quantum Design Physical Properties Measurement System (PPMS). In order to measure mechanical behavior of the films, a Hysitron Triboindenter fitted with a Berkovich diamond indenter was used. The tip radius was approximately 100 nm, giving accurate indentation data via calibration of the tip area function on fused silica at contact depths of 30 nm and greater. The film tested via nanoindentation was over 100 nm in thickness, so indentation data at contact depths between 30 nm and 50 nm was used to avoid substrate effects.

Figure S1: X-ray diffraction (XRD) patterns of VC, TiC, and TaC thin films on sapphire substrates.

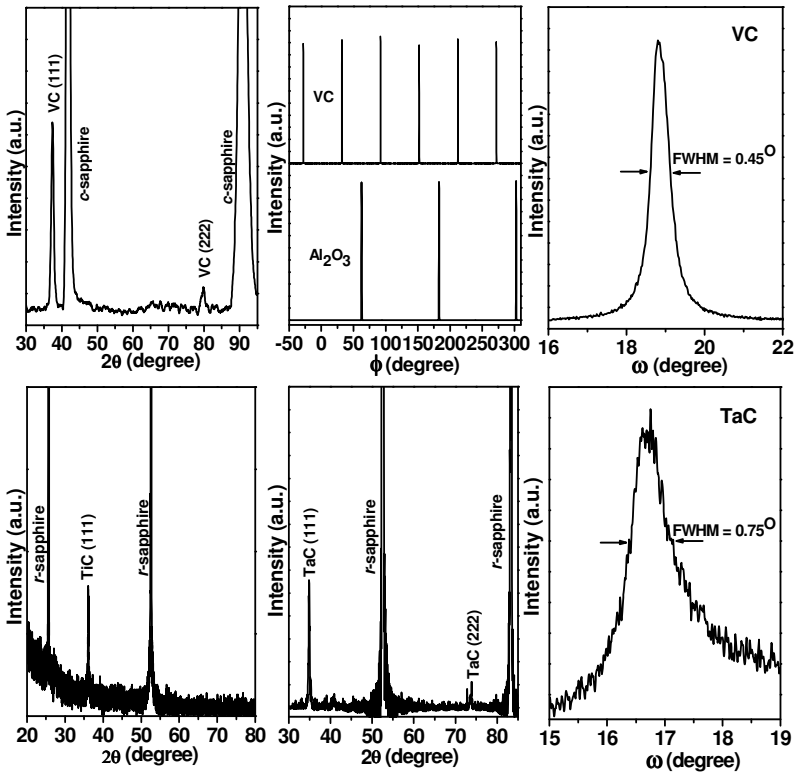

Figure S2: Scanning electron microscopy (SEM) images of the TiC film.

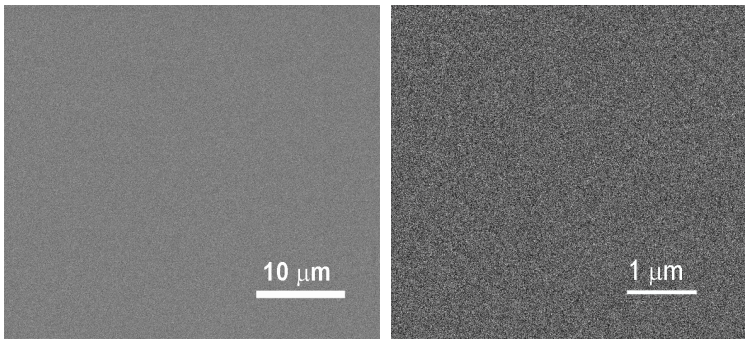

Figure S3: TEM and HRTEM images of a TiC film on an *r*-plane sapphire substrate.