Spontaneous Short-Range Ordering in Artificial Mo/V(001) Superlattices with Modulation Periods < 2 Monolayers

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Metallic transition metal multilayers and superlattices are important systems in applications such as soft X-ray mirrors, magnetic recording, and hydrogen storage. They have also played an important role as model systems to understand the growth processes of multilayers and superlattices in general. The bcc Mo/V system has been used as such a model system since it can readily bee grown as high quality superlattices with periodicities in the range 2-50 monolayers[1] with almost atomically abrupt interfaces.[2]

In this work we challenge the concept of chemical modulation in superlattices by the growth of periodicities shorter than 2 monolayers (i.e., < one unit cell in the bcc structure) by UHV magnetron sputter epitaxy onto (001)-oriented MgO. Five Mo_m/V_n superlattices were grown: $Mo_{1.230}/V_{1.251}$, $Mo_{1.230}/V_{0.834}$, $Mo_{0.820}/V_{0.834}$, $Mo_{0.820}/V_{0.417}$, and $Mo_{0.410}/V_{0.417}$ where m and n denotes the nominal numbers of crystalline (001) monolayers of Mo and V, respectively, in each layer. Also, one $Mo_{0.5}V_{0.5}$ alloy crystal was grown for reference. The growth was carried out to a thickness of 500 nm at a substrate temperature of 700°C in a pure Ar (99.999999%) sputtering gas atmosphere at 5 mTorr.

XRD Bragg-Brentano scans revealed superlattice peaks occurring at the positions of supra-periods defined by the beating of the spatial frequencies of the crystalline unit cell periodicity and the incommensurate chemical modulation periods as described by Shuller et al..[3] The XRD data confirmed the designed chemical modulation in the growth direction of the $Mo_{1.230}/V_{1.251}$, $Mo_{1.230}/V_{0.834}$, $Mo_{0.820}/V_{0.834}$, and $Mo_{0.410}/V_{0.417}$ superlattices showing that the superlattices grow in a layer-by-layer mode even if each layer is thinner than half a monolayer. In addition, the $Mo_{0.820}/V_{0.834}$, superlattice exhibited a clear XRD peak at the, in bcc forbidden, 001 position indicating short-range ordering af the Mo and V.

The XRD data of the superlattices were successfully simulated using the GenX code,[4] modified to allow for modeling of short range ordering as well as supra-periodicity. The modeling suggest that the short range ordering in the $Mo_{0.820}/V_{0.834}$occur as dispersed, nm-sized, domains in which Mo and V occupy nearest neighbor sites.

High resolution cross-sectional TEM clearly showed the contrast of the supra-periodicity in real-space lattice-resolved imaging of the $Mo_{0.820}/V_{0.834}$ superlattice and selected area diffraction (SAED) patterns showed clear spots at the positions of the forbidden bcc peaks (h+k+l odd) indicating a CsCl structure. Moreover, the [110] zone-axis SAED of the $Mo_{0.820}/V_{0.834}$ superlattices exhibited diffuse but clear diffraction features around the forbidden bcc peaks. Dark field imaging from this diffuse scattering revealed tiny preciptates, less than 1 nm in size. evenly dispersed in the crystal.

In conclusion, Mo/V superlattices with periodicities well below the unit cell size can be grown. When both layers are nearly half a monolayer thick, the experimental evidence combined with the XRD modeling points at the following growth model: When sub-monolayer layers of Mo and V are epitaxially grown by layer-by-layer mode, the atoms self-organize by preferably attaching to unlike atoms which leads to formation of sub-nm-sized clusters of a new $Mo_{0.5}V_{0.5}$ phase dispersed in a single crystal supra-lattice.

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