Thin-film growth of the charge-density-wave oxide $Rb_{0.30}MoO_3$

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We report on the thin-film fabrication of a charge-density wave (CDW) compound. Single-phase epitaxial films of the model CDW oxide $Rb_{0.30}MoO_3$ have been grown by pulsed-laser deposition. Detailed analyses show that the $Rb_{0.30}MoO_3$ films have μm-size grains with the CDW chains oriented parallel to the substrate. On $SrTiO_3$ (510), the CDW chains align into a single direction within the film plane. The electrical resistance of the films demonstrates a CDW state below about 182 K. Structures patterned in films will permit unprecedented studies of phase-coherent CDW transport, as well as the exploration of devices based on CDWs. © *1996 American Institute of Physics.* [S0003-6951(96)02226-7]

Electrical conductors with a chain-like structure may exhibit a phase transition to a collective ground state with charge-density waves (CDWs).[1] The appearance of a CDW state is connected to the Peierls instability[2]: at low temperatures the uniform distribution of conduction electrons of a one-dimensional (1D) conductor is unstable due to their coupling to phonon modes. As a result, the lattice of atoms is distorted and the electrons condense into a ground state with a periodic modulation of the charge density. Collective transport occurs when these CDWs slide along the chains. To date, CDW transport has been studied in bulk crystals and has shown many remarkable phenomena. Examples are ac current oscillations induced by a dc electric field and strongly nonlinear electrical properties. The strongly nonlinear behavior at low fields and the fact that CDW polarization leads to extremely high dielectric constants ranging from $>10^8$ at low frequencies to $\sim 10^3$ at microwave frequencies, are of interest for possible applications. The first three-terminal CDW device[3] has recently been fabricated, but integration in applications seems difficult since it was made out of a bulk crystal.

The sliding motion of CDWs shows many similarities with transport in superconductors, with the role of current and voltage reversed. For example, a current-frequency relation exists for the collective CDW current, analogous to the ac Josephson relation between voltage and frequency in superconductors. Thin-film devices with Josephson junctions are very important in both fundamental studies and applications of superconductivity. Such devices are unexplored for CDW systems due to the absence of CDW thin films.

We have achieved thin-film growth of the oxide $Rb_{0.30}MoO_3$ ("blue bronze"). The bulk properties of this model CDW compound have been well studied.[4,5] $Rb_{0.30}MoO_3$ has a monoclinic crystal structure with 1D CDW chains built of clusters of MoO_6. The chains are aligned along the *b*-axis of $Rb_{0.30}MoO_3$. $Rb_{0.30}MoO_3$ exhibits a CDW state below a Peierls temperature of 182 K. The wavelength of the CDW is ~1 nm and is incommensurate with the underlying lattice.

For the growth of $Rb_{0.30}MoO_3$ films, we have used a pulsed-laser-deposition[6] system which was developed for epitaxial growth of $YBa_2Cu_3O_7$ films. In a vacuum chamber to which oxygen has been supplied, a pulsed excimer-laser beam hits a polycrystalline $Rb_{0.30}MoO_3$ pellet. Subsequently, material is transferred to a substrate which is mounted opposite to this target.

We find that blue bronze films can be grown at oxygen pressures from 100 to 200 mTorr and substrate temperatures between 350 and 500 °C. Films grown in this region are blue and conducting at room temperature. Elemental composition Rb:Mo:O amounts to 0.30:1:3 to within an accuracy of 10%, as found from energy-dispersive analysis of x rays (EDX). Typical deposition rates and film thicknesses are 0.1–1 nm/s and 100–1000 nm, respectively.

X-ray diffraction has been used to determine the orientation of crystal planes parallel to the substrate. A typical example of a θ–2θ scan of a blue bronze film is shown in Fig. 1. From these data, it appears that the film is essentially single-phase $Rb_{0.30}MoO_3$. The main diffraction peak is $(\bar{2}01)$, which shows that the CDW chains — which are aligned within the $(\bar{2}01)$ planes — are directed parallel to the substrate surface. Three other grain orientations are also visible, but their intensity is at least one order of magnitude lower than the $(\bar{2}01)$ peak. As expected from the crystal structure of $SrTiO_3$ (STO), substrate peaks appear at 22.78° and 46.49°; the small peak at 42.0° is a K_β satellite of the STO (200) peak.

Film morphology has been studied by use of scanning-electron microscopy (SEM) and atomic-force microscopy (AFM). Films appear to be granular with grain sizes of the order of 1 μm. Grains on sapphire–Al_2O_3 (012)–substrates have an oval to rectangular shape and are oriented randomly on the substrate surface [Fig. 2(a)]. On $SrTiO_3$ substrates, the grains have elongated shapes and they are oriented within the substrate plane [Figs. 2(b) and 2(c)]. AFM studies show similar grain structures. Surface corrugation is substantial, i.e., of the order of 50 nm for films grown at 375 °C and 150 nm for films grown at 440 °C. Grain size

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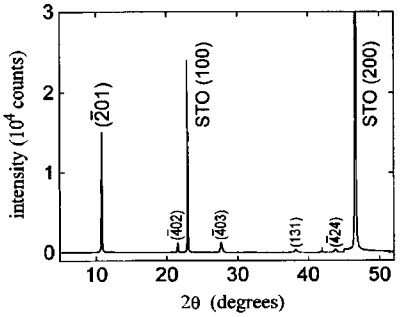

FIG. 1. X-ray $\theta-2\theta$ diffraction pattern of a $Rb_{0.30}MoO_3$ film deposited on a $SrTiO_3$ (100) substrate at 440 °C and 120 mTorr. The dominant peak of the $Rb_{0.30}MoO_3$ film at 10.60° arises from diffraction of the ($\bar{2}01$) planes which contain the CDW chains.

and corrugation increase with increasing substrate temperature and with decreasing deposition rates.

The absence of oriented grains on sapphire can be understood from results of high-resolution transmission electron microscopy (TEM). TEM images show that an amorphous 30 nm thick AlO_x layer has formed at the interface of the Al_2O_3 (012) substrate and the blue bronze film. Prior to film deposition, the Al_2O_3 (012) substrate surface is crystalline. Thus, during deposition a chemical reaction occurs between Al_2O_3 and $Rb_{0.30}MoO_3$, which prevents epitaxial growth. Consequently, ($\bar{2}01$) grains will grow with a random inplane orientation of the b axis.

The grain orientation seen in Fig. 2(b) strongly suggests heteroepitaxial growth on the $SrTiO_3$ (100) substrate. SEM and AFM studies cannot conclusively deduce the orientation of the CDW chains within the plane. With x-ray ϕ-scan analyses, one can relate the orientation of the CDW chains to the underlying substrate lattice. For the (100) substrates, we find that the CDW chains run parallel to either the [010] or the [001] $SrTiO_3$ axes.[7] This 90° symmetry is explained from the square symmetry of the $SrTiO_3$ (100) surface. The lattice parameter along the [010] and [001] directions of this surface is 0.391 nm yielding a mismatch of 3.3% with half of the length of the blue bronze CDW axis (0.756 nm).

Figure 2(c) shows that the grains can be preferentially aligned into a single direction by use of the (510) cut of $SrTiO_3$. This substrate features a rectangular surface unit cell with lattice parameters of 0.391 nm along [001] and 1.991 nm along [$\bar{1}$50]. With the ($\bar{2}01$) planes parallel to the (510) substrate, the distance of 1.991 nm features a 0.6% mismatch with the blue bronze unit cell in the direction perpendicular to the CDW axis. X-ray ϕ-scans show that 90% of the blue bronze grains indeed have the CDW axis aligned along the $SrTiO_3$ [001] direction.

Epitaxial growth on $SrTiO_3$ (100) is verified by TEM as illustrated in Fig. 3. A sharp interface between substrate and blue bronze film is observed. Using the distance between substrate plane (0.391 nm) as an internal calibration, the distance between the planes in the blue bronze film is measured to be 0.84 ± 0.02 nm, in agreement with the expected distance between neighboring ($\bar{2}01$) planes of 0.83 nm.

The temperature dependence of the electrical resistance of a blue bronze film is shown in Fig. 4. Gold pads, 500

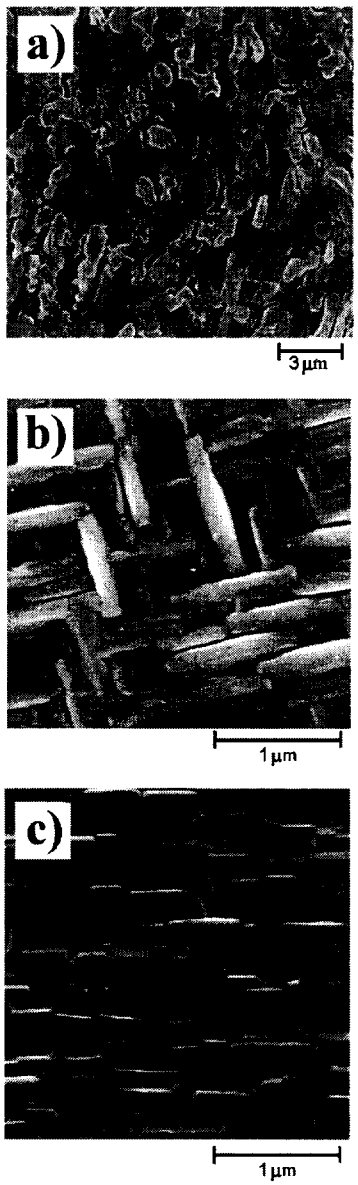

FIG. 2. Scanning-electron microscopy photographs of $Rb_{0.30}MoO_3$ films grown (a) on Al_2O_3 (012) (sapphire), (b) on $SrTiO_3$ (100), and (c) on $SrTiO_3$ (510). The rectangular substrate surface of $SrTiO_3$ (510) enforces unidirectional growth of grains.

μm apart, were evaporated to contact the blue bronze film. Wires were ultrasonically bonded to the gold pads. The room-temperature resistance of 45 Ω corresponds to a resistivity of a few mΩ cm.

Below about 182 K, a pronounced increase of the film resistance is observed, consistent with the opening of a gap at the Peierls temperature. The transition near 182 K appears to be smoother than in bulk crystals. This may be an intrinsic effect connected to the film thickness[8] or due to the granular nature of the film. Below 182 K, the film resistance shows the expected thermally activated behavior due to quasiparticle excitations. From a fit to $R\propto\exp[\Delta(T)/k_BT]$, we find a zero-temperature energy gap of 470 K. Here, $\Delta(T)$ is cal-

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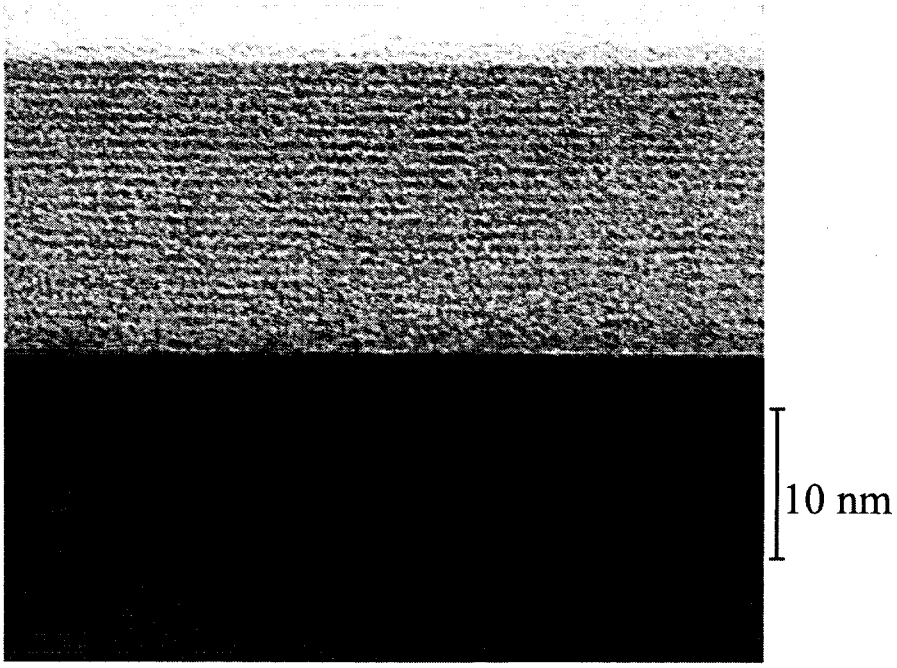

FIG. 3. A high-resolution transmission-electron microscopy image showing a sharp interface between a $Rb_{0.30}MoO_3$ thin film on top of a $SrTiO_3$ (100) substrate. The image has been taken along the (011) direction of $SrTiO_3$.

culated according to the BCS theory. Both the Peierls temperature and energy gap agree with data on bulk crystals.[4,5,9]

The present work reports the first growth of thin films of a CDW compound. If the film thickness can be controlled at the level of monolayers, heterostructures may be grown with normal, superconducting, or semiconducting materials. By use of lithographic techniques, films can be patterned to form well-defined microstructures. Submicron structures will provide new possibilities for the study of microscopic aspects of the physics of charge-density waves. Fabricated structures are a necessary condition for practical applications of CDWs.

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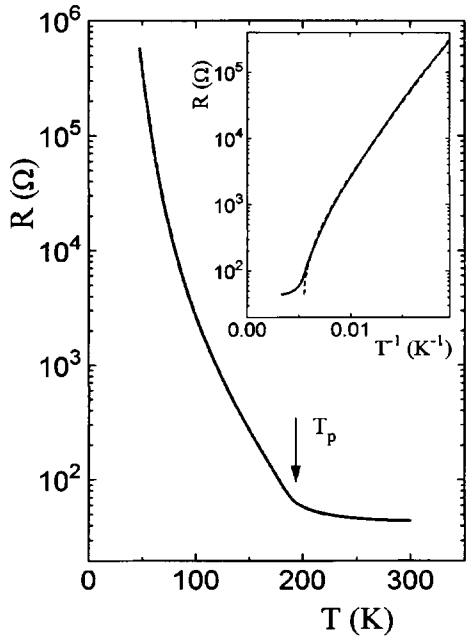

FIG. 4. Resistance vs temperature of a blue bronze film grown on an Al_2O_3 (012) substrate at 460 °C and 135 mTorr showing a strong increase of the resistance below the Peierls temperature T_p of about 182 K. The inset shows an activation plot for the resistance. The dashed line denotes a fit to $R \propto \exp[\Delta(T)/k_BT]$.

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