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Oriented Epitaxial Films of (NMP) (TCNQ)

Abstract: An important step in the characterization of organic conductors is the ability to correlate the solid state electrical properties of these materials with their composition and crystal structure. In many cases it has not been possible to grow single crystals of suitable size or purity for such investigations. The use of epitaxial films represents an alternative approach. In addition, such films may be potentially useful as larger area conductive surfaces. This paper describes the preparation of relatively large-area, oriented epitaxial films of the organic conductor N-methylphenazinium-7,7,8,8-tetracyanoquinodimethanide (NMP) (TCNQ) by means of vacuum evaporation. Factors that appear to affect the degree of orientation, the film areas, and the chemical composition include the source temperature, the kind of evaporation (rapid or slow), the degree of lattice matching between the substrate and the organic material, and the substrate surface charge potential.

Introduction

A great deal of research has been done in efforts to successfully correlate the solid state electrical properties of various organic conductors with their chemical composition and crystal structure. Such correlations have been found for the salts of tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) and other closely related derivatives [1, 2]. For instance, the highly conductive form of (TTF) (TCNQ), as compared with other typically insulating simple salts of (TCNQ), is attributed to its unique stacked, columnar crystal structure, and to the various inter- and intra-chain electronic interactions (couplings) which lead to partial charge transfer between the separate donor and acceptor stacks.

The salt N-methylphenazinium tetracyanoquinodimethanide (NMP) (TCNQ) is yet another organic conductor currently under investigation. It is a particularly useful prototype for distinguishing between inter- and intra-molecular transitions by means of optical polarization measurements [3(a)]. The salt (NMP) (TCNQ) has also been used in investigations of the special spectroscopic features of an ordered polyatomic system and its line-shape dependence on the direction of polarization [3(b), 4]. Such studies, because of instrumental limitations, require relatively uniform homogeneous phase, extremely pure samples that have areas of 5 to 10 mm^2. In the majority of cases it is not possible to obtain single crystals that meet these material and dimensional requirements. Epitaxial films offer a means of obtaining single-crystal-like structures of high purity (no solvent inclusions) for these investigations.

Because of certain similarities in the crystal structures of (TTF) (TCNQ) and (NMP) (TCNQ), and because of our previous success in producing epitaxial films of (TTF) (TCNQ) [5], we initiated work on the preparation of similar epitaxial films of (NMP) (TCNQ).

(TTF) (TCNQ) crystallizes in a monoclinic form [6], the lattice constants being a = 1.13 nm (11.30 Å), b = 0.382 nm (3.82 Å), c = 1.847 nm (18.47 Å), $\alpha = \gamma = 90°$, $\beta = 104.4°$. The stacking axis for the segregated (TTF) and (TCNQ) radical ions is the $\langle 010 \rangle$ direction. There are two known crystal phases of (NMP) (TCNQ), one conducting [7] and the other insulating [8]. It has been shown [7] in the high conductivity (NMP) (TCNQ) that the (TCNQ)$^-$ ions pack in a similar columnar fashion along the $\langle 100 \rangle$ direction with a very short interplanar spacing (0.326 nm). This form of (NMP) (TCNQ) crystallizes in a triclinic lattice with constants a = 0.387 nm, b = 0.778 nm, c = 1.574 nm, $\alpha = 91.67°$, $\beta = 92.67°$, $\gamma = 95.38°$, and is obtained as black crystals which appear green (in transmission) in thin sections.

There are also certain similarities in the physical properties of (NMP) (TCNQ) and (TTF) (TCNQ). For instance, both materials have a higher electrical conductivity and optical absorption along their columnar

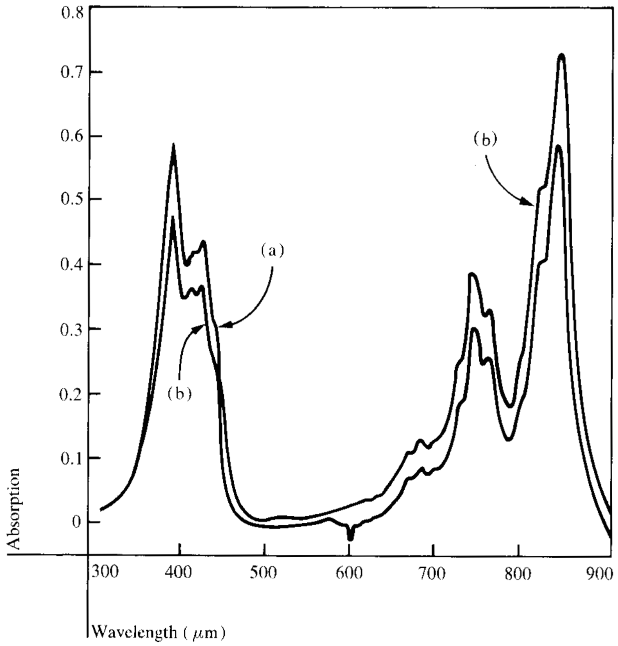


Figure 1 Solution optical absorption spectra of (NMP) (TCNQ) in acetonitrile (a) 1 : 1 crystalline salt, (b) 1 : 1 evaporated film, dissolved.

axes. These features, which are a manifestation of the structural similarity between the two salts, led to the belief that oriented films of (NMP) (TCNQ) could be prepared with techniques similar to those developed for (TTF) (TCNQ), and that the orientation of such films could be observed optically.

In our previous work on epitaxial films of (TTF) (TCNQ) on (100) faces of NaCl it was established that the epitaxial relation is $\langle 010 \rangle_{(\mathrm{TTF})\,(\mathrm{TCNQ})} \parallel \langle 110 \rangle_{(\mathrm{NaCl})}$, and that the lattice mismatch is 4.4 percent. Several examples of organic epitaxy have demonstrated that lattice mismatch of this order or larger does not prevent epitaxial film growth [9]. The expectation of a similar relation (that is, a stacking axis parallel to a principal direction of the substrate lattice), and the knowledge that the lattice mismatch is only 2.8 percent in the case of (NMP) (TCNQ), led to the repeated use of NaCl as a substrate. For (NMP) (TCNQ), the expected epitaxial relation is $\langle 100 \rangle_{(\mathrm{NMP})\,(\mathrm{TCNQ})} \parallel \langle 110 \rangle_{(\mathrm{NaCl})}$.

Triglycine sulfate (TGS) was used as a substrate in order to determine whether free surface charges enhance preferential-texturelike depositions *independently* of lattice match, as is believed to be the case for (TTF) (TCNQ) [5]. In addition, stressed surfaces of NaCl were used as a means of creating surface charges, and thereby served as a means to observe any enhancement of film orientation and/or uniformity where the same degree of lattice match was present.

Experimental procedure

Crystalline 1 : 1 (NMP) (TCNQ) [10] was used for all evaporations. The substrates used were cleaved (100) NaCl, surface distorted (100) NaCl (compressed in either the ⟨110⟩ or ⟨100⟩ direction), polished (211) NaCl, and cleaved (010) TGS [11]. The TGS was unpoled and undoped. Poling of the TGS was not necessary because the (010) TGS surface was 75 percent singly oriented, with lens-shaped domains that were on the average 0.1 to 0.5 mm in diameter.

A standard evaporation unit was used, with a maximum vacuum capability of 10^{-6} Pa (10^{-8} torr). The evaporation source was of the cylindrical (chimney) type. The distance from source to substrate was 3 cm. The substrate holder and shutter could be water cooled; hence the substrate temperature was kept constant within 2 to 3°, as measured by thermocouples, and was maintained at 293 ± 3 K. The source temperature, as measured by a thermocouple that was spring-loaded at the base, was determined to within ±0.5 K. The evaporation material was used sparingly and was evenly dispersed over the bottom surface of the source in order to achieve complete thermal equilibrium over the entire mass. In experiments where the rapid evaporation technique [12] was used, the material was heated either by dropping it onto the preheated source or by raising the source temperature rapidly. In the slow evaporation technique, the source (with material) was heated from room temperature to the prescribed temperature slowly, over 20 to 30 minutes. The pressure was monitored during evaporation and was maintained at 10^{-3} to 10^{-5} Pa. It was not possible to measure the actual rate of evaporation because of the geometrical relationship between the chimney-type source and the substrate; however, the rate could be estimated from the thickness measurements. These rates were approximately 20–30 nm/min for the rapid case and approximately 5 nm/min for the slow evaporations.

Film thicknesses were either measured by interferometry (films ≤ 50 nm thick, where the surface roughness did not prevent the deposition of highly reflective metal films on top of the organic), or estimated from the optical absorption spectra (films 50–150 nm thick), as measured in the solution phase (acetonitrile solvent) by dissolving the evaporated (NMP) (TCNQ) off the substrates. The absorption coefficient of (NMP) (TCNQ) is approximately 10^5 cm^{-1} at 870 nm [4]. Film thicknesses measured optically are accurate to within ±10 percent.

Instruments used to observe the area, uniformity, structure, orientation, and composition of the films included a polarizing microscope (using transmitted light), a Phillips x-ray diffractometer, a Perkin-Elmer 301 grating infrared spectrometer, and an AEI-802 standard high voltage electron microscope. The ultraviolet and visible absorption spectra were run on a Cary 14 spectrometer.

Results and discussion

The film preparation conditions are summarized in Table 1. They indicate that pure 1 : 1 (NMP) (TCNQ) films are formed by a rapid evaporation technique under a vacuum of 10^{-4} to 10^{-6} Pa, while the source temperature is maintained between 363 and 408 K. The rate of evaporation (rapid or slow) and the source temperature determine the composition, uniformity, and purity of the films obtained.

The chemical composition of the films was checked by taking the optical absorption spectra in the solution phase. The stoichiometry of the oriented epitaxial films used for further studies was verified; these films were found to have a 1 : 1 (NMP) (TCNQ) composition by comparison of the solution absorption spectrum obtained for known 1 : 1 (NMP) (TCNQ) [13, 14] with that for a solution of the deposited film dissolved in acetonitrile. The spectra were essentially identical and are shown in Fig. 1. Compositional changes would have been indicated by variations in the ratio of optical absorption peak heights [15] at the following wavelengths: 395 nm/842 nm, 420 nm/842 nm, and 420 nm/395 nm. Although there is some overlap of the peaks, in general, maxima at 395, 420, and 842 nm could be used as a measure of the amounts of $(\text{NMP})^+$, $(\text{TCNQ})^0$, and $(\text{TCNQ})^-$, respectively [13, 14] to within ± 10 percent. In control experiments with polycrystalline 1 : 1 (NMP) (TCNQ) evaporant, the values of the ratios mentioned above were 0.82–0.84, 0.59-0.61, and 0.71-0.74, respectively. Note that (NMP) (TCNQ) is approximately 70 percent ionized in acetonitrile solution [14]. Data taken on any film that did not possess an identical absorption spectrum were not used. It should also be noted that the ratios were determined to be independent of solution concentration over the range of our experiments (2-3 × 10^{-5} moles/liter).

Stoichiometric films are obtained by a rapid evaporation (which occurs between 363 and 403 K), apparently by ensuring the presence of sufficient and equal concentrations of both NMP and TCNQ molecules for stoichiometric salt formation at the substrate surface. Temperatures much greater than 403 K lead to thermal decomposition of the source material, with subsequent deposition of degraded materials on the films. Temperatures below 343 K give no deposition. When the rate of evaporation is very slow (about 6 nm/min), fractional distillation (alteration of theoretical peak ratios) occurs and randomly oriented films are also obtained. Random orientation can be observed both by x-ray diffraction and by examination under a polarizing microscope. Increasing the internal pressure during the evaporation was found to give (NMP) (TCNQ) films whose absorption spectra were inconsistent with the 1 : 1 evaporant spectrum (see Table 1).

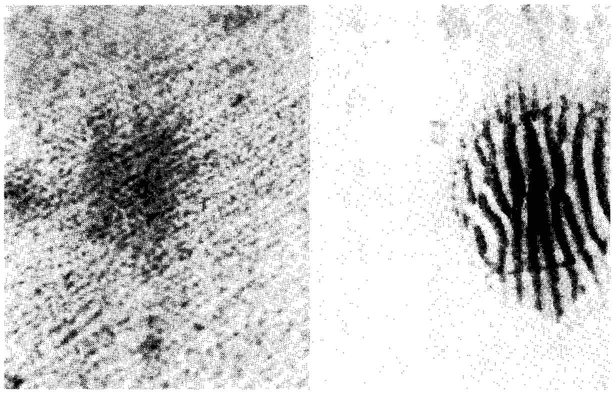
Table 1 (NMP) (TCNQ) film preparation conditions.

Source temperature (K)	*Pressure* (Pa)	*Evaporation method* *Slow*	*Rapid*	*Results*
<343	10^{-3} to 10^{-6}	X	X	No deposition
≈343	10^{-4} to 10^{-6}	X		Nonstoichiometric
363 ≤ T ≤ 408	10^{-4} to 10^{-6}		X	1 : 1 Composition
343 ≤ T ≤ 408	10^{-3}	X	X	Nonstoichiometric
408 ≤ T ≤ 433	10^{-4} to 10^{-6}	X	X	Decomposition begins
>433	10^{-4} to 10^{-6}	X	X	Decomposed

Table 2 Typical results of the effect of substrate on the epitaxy and orientation of (NMP) (TCNQ) films ranging in thickness from 15-150 nm.

Substrate	*Nature of films*	*Maximum area of uniform deposition*
Cleaved NaCl (100) face	Doubly oriented	Very small domains (2 × 2 μm) over whole substrate surface
Cleaved NaCl (100) face compressed along ⟨100⟩	60–70 percent preferentially singly oriented	1-10 mm^2
Cleaved NaCl (100) face compressed along ⟨110⟩	70–80 percent preferentially singly oriented	1 mm^2
Polished NaCl (211) face	No singly oriented areas	——
Cleaved TGS (010) face	Domains decorated by singly oriented areas	10^{-2} mm^2

Table 2 summarizes structural data, as observed under a polarizing microscope, for typical (NMP) (TCNQ) films deposited on various substrate materials and surfaces. (NMP) (TCNQ) absorbs strongly parallel to its high conductivity ⟨100⟩ axis; therefore photographs of these films (Figs. 2–4), as observed under transmitted polarized light, can be used to determine orientational uniformity. The patterns of light and dark indicate microdomain orientations. It is seen that the size of the domains as well as the degree of orientation is affected by the choice of substrate material. Doubly oriented films were obtained on cleaved (100) NaCl, this being due to the fact that two similar ⟨110⟩ directions are present in the (100) NaCl surface. However, films deposited on polished



(a) (b)

Figure 2 (NMP) (TCNQ) films under transmitted polarized light (TPL). Film area is approximately 3–4 × 10^{-3} mm^2. (a) Doubly oriented microdomains obtained on cleaved (100) NaCl. (b) Cleaved (010) TGS substrate. Note the lens-shaped domains (charged) decorated by singly oriented areas.

(211) NaCl (2.8 percent lattice mismatch) showed a poor orienting effect *despite* a single ⟨110⟩ direction in the substrate surface. It is unclear whether this was due to the random and not particularly dense nucleation centers and/or to surface damage that occurred during polishing of the substrates. We have also observed that the probability of single-crystal film formation is greater when (NMP) (TCNQ) is evaporated onto NaCl, as compared to evaporation onto CaF_2, where the lattice mismatch is less than one percent in the ⟨110⟩ direction.

The greatest degree of single orientation (70 to 80 percent) was obtained on substrates of cleaved (100) NaCl that were compressed along the ⟨110⟩ axis. On the other hand, the maximum area of uniform deposition (10 mm^2) occurred on substrates of cleaved (100) NaCl that had been compressed along the ⟨100⟩ axis. In addition, it can be seen in Fig. 3 that orientation is enhanced considerably near the cleavage steps in the substrate crystal face and at charged domains in TGS [Fig. 2(b)].

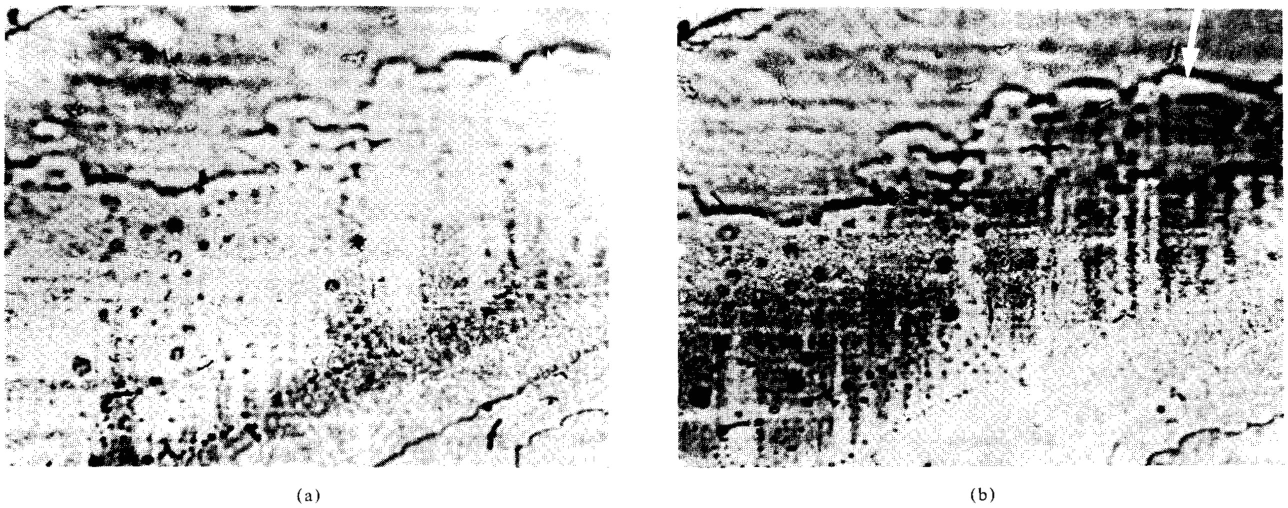
These results can be interpreted in terms of the relative effects of lattice mismatch and surface charge on the substrate. Minimizing the lattice mismatch should increase the probability of uniform orientation of the organic film upon the substrate. However, the amount of surface charge potential that is present seems to play an even more important role in orienting the films, perhaps both because the TCNQ groups are highly polarizable and because of the strong tendency for TCNQ to form anions. This may explain the rather poor film orientation obtained for (211) NaCl substrates. It is known that compression of NaCl crystals can affect the surface potential [16, 17]. In addition, nucleation in epitaxy is known to occur mostly at spots of potential jumps in the surface. The better oriented deposits are indeed obtained on NaCl crystals which have been compressed and on the charged domains of TGS. Thus, it appears that lattice match may be of only secondary importance when a high surface potential is present. This could also explain the preferential deposits on charged TGS domains [Fig. 2(b)], where there is a very poor lattice match.

Investigations of the structure of the deposited films of (NMP) (TCNQ) by electron diffraction proved to be very difficult because of the susceptibility of the films to beam and heat damage. The occurrence of the former is more probable, as was demonstrated by later experiments using a liquid nitrogen cooled substrate holder. At the beginning of the observation the electron diffraction pattern consisted mainly of spot patterns, but after initial degradation the pattern remained stable. If the beam intensity was further increased the material began to decompose, changing to a form that gave an electron diffraction pattern consisting of amorphous haloes. Evaluation of the electron diffraction pattern was possible, however, if care was taken not to expose the films for a long time.

Three points have been determined from this investigation. First, the values given by Melby [13] for the angles and axes (unit cell values) in single crystals of (NMP) (TCNQ) gave the best fit to the electron diffraction patterns obtained on our deposited 1 : 1 (NMP) (TCNQ) films when the preceding experimental cautions were observed. In addition, the patterns indicate a preferential orientation of the deposits, the orientational mismatch between adjacent single-crystalline areas being less than ten degrees. Finally, the ⟨001⟩ direction is found to lie in the plane of the substrate. From these data, however, it was not possible to determine whether it is the ⟨100⟩ or the ⟨010⟩ direction that lies parallel to the substrate plane.

The x-ray diffraction spectra were also useful in determining the orientation of the (NMP) (TCNQ) films, but there were limitations as to the conclusions that could be drawn, as will be discussed. The diffraction patterns of highly oriented deposited films show one strong reflection and a possible second weaker reflection. These peaks most likely correspond to the (010) and (020) reflections, respectively. The assignment of the peaks is, however, ambiguous because of possible angle shifts caused by the facts that 1) the films themselves are not absolutely flat to begin with (substrates are buckled and contain cleavage steps), and 2) the technique used for transferring the films (floating with water) can leave the films lying at an angle to the glass plates onto which they are transferred.

Returning to a comparison with (TTF) (TCNQ), recall that in both materials the TCNQ radical ions stack in a columnar fashion along the high conductivity axis, and for the (TTF) (TCNQ) case, it has been shown unequivocally that this axis lies in the plane of the substrate [5]. In addition, the optical anisotropy observed in (TTF)



(a) (b)

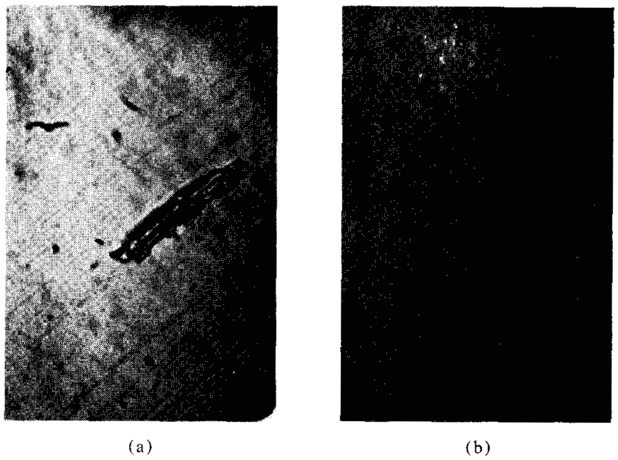
Figure 3 Singly oriented areas of (NMP) (TCNQ) on cleaved (100) NaCl compressed along the ⟨100⟩ axis, as observed under TPL. Film area is 2.8×10^{-2} mm². Polarizer-analyzer angle set at (a) 0°, (b) 90°. Arrows point out preferential orientation at the cleavage step.

(TCNQ) shows the strongest absorption along this conducting axis. Our oriented epitaxial (NMP) (TCNQ) films possess the same type of optical anisotropy.

There are also preliminary infrared data on these (NMP) (TCNQ) films [4] that show lineshape changes dependent upon the direction of polarization.

Thus, when all the experimental data are considered as a whole, we believe it is most likely that it is the (010) plane of the (NMP) (TCNQ) films that lies parallel to the substrate surface.

As in the case of (TTF) (TCNQ) [4], there is a certain thickness limit above which the singly oriented films become randomly oriented. In the (NMP) (TCNQ) films this limit is approximately 150 nm. This may be related to the growth habit of (NMP) (TCNQ) of easily forming twins in the ⟨100⟩ direction, as actually observed by us in electron diffraction patterns of thick films. Surface irregularities, as well as lattice mismatch, may also enhance twin formation, and these twins could serve as additional nucleation centers, creating polycrystalline, randomly oriented material.



(a) (b)

Figure 4 Singly oriented (NMP) (TCNQ) film on cleaved (100) NaCl compressed along the ⟨110⟩ axis, as observed under TPL. Film area is 1.4×10^{-2} mm². Polarizer-analyzer angle set at (a) 0° and (b) 90°. The large darker object is a dust particle, whose location varied.

Summary

Highly oriented 1 : 1 (NMP) (TNCQ) films up to 150 nm thick, which are useful for optical investigations, have been successfully prepared by controlling both the evaporation conditions and the substrate material. The optimum evaporation conditions include a rapid technique, a source temperature between 343 and 408 K, a film thickness less than 150 nm, and an internal pressure of 10^{-4} to 10^{-6} Pa during the evaporation. Choice of the best substrate material involved minimizing the lattice mismatch, the best readily available material being cleaved (100) NaCl. Epitaxial film growth and the degree of uniform orientation were optimized by additionally increasing the surface potential of the best substrate by means of compression. A 70 to 80 percent preferentially singly oriented film was obtained on (100) NaCl that had been stressed along the ⟨110⟩ axis. The maximum area of uniform orientation occurred for (100) NaCl substrates compressed along the ⟨100⟩ axis. In this case, although there was only 60 to 70 percent preferentially singly oriented material, the film areas were as high as 10 mm^2, compared with approximately 1 mm^2 in the previously mentioned films.

One of the particular advantages of these films is the facility with which the uniformity of the orientations can be determined by using simple optical absorption techniques because of the anisotropy of the electronic absorption. In addition, since NaCl dissolves in water, the films can easily be examined by electron diffraction techniques after they have been floated off the substrates. The preparation of these large-area (compared with single crystals) epitaxial films is relatively easy and far less time-consuming than normal single-crystal growth techniques. One also avoids solvent contamination, which invariably occurs in crystal growth.

Additional work, for instance, in varying the substrate temperature during the evaporation, or in the use of an electric field to enhance orientation, may yield films which co-maximize the degree of uniform orientation and the film area.

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