Increased photo- and electroluminescence by zone annealing of spin-coated and vacuum-sublimed amorphous films producing crystalline thin films

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Spin-coated and vacuum sublimed amorphous thin films ($\sim$100 nm thick) were converted into single crystalline films with a simple moving-zone-annealing technique, in which a heated metal wire generated a narrow annealed zone in the film as it is moved across the sample. This annealing resulted in both the photoluminescence and electroluminescence to increase dramatically (by 3–4 times), for example with $Ru(bpy)_3(ClO_4)_2$ and aluminum 8-hydroxyquinoline, (Alq_3), as light emitting devices. This technique is of interest in improving the behavior of highly luminescent thin film optoelectronic devices. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1636823]

Thin films ($\sim$100 nm thick) are used in many optoelectronic devices since photons can easily penetrate through these without suffering large absorption losses. Single crystalline thin films often offer better properties in devices, but are more difficult to grow. Molecular beam epitaxy, for example, operates in ultrahigh vacuum chamber (10^{-10}–10^{-11} Torr) and has severe limitations on the substrate selection due to the requirement of lattice match.[1] On the other hand, widely used low cost techniques such as spin coating and vacuum sublimation produce thin films that are generally amorphous with compromised properties. Here, we describe a simple method of moving-zone annealing to convert spin-coated and vacuum deposited amorphous thin films into single crystalline ones. In this method, an electrically heated thin wire produces a narrow annealing zone on the coated film, which is moved from one end of the sample to other. After a single pass, the amorphous material became a single crystal thin film that showed significantly improved photo- and electroluminescence.

The method originates from our recent work on *in situ* regrowth and purification of organic single crystal thin films of interest in memory and photovoltaic applications.[2] In this case, films were sandwiched between two indium-tin oxide (ITO)-coated glass pieces. When a molten zone on the film was generated by a heated metal wire and moved across the sample, the film became more crystalline and was purified. We now extend this method to films with one open surface that can be prepared with conventional techniques such as spin coating and vacuum sublimation. Importantly, the temperature at the moving zone could be significantly lower than the melting point of the film, and therefore, widening its application to those materials without a convenient melting point such as many organic compounds that decompose at high temperature before melting. In the experiment, substrates such as a piece of glass or an ITO-coated glass cover slip directly contacted a Pt heating wire (127 μm in diameter) and moved at a fixed rate with an inchworm motor (Burleigh) under ambient condition as shown in Fig. 1(a).

As an example, here we describe treatment of spin coated films of $Ru(bpy)_3(ClO_4)_2$ that have been used in light emitting devices (LEDs).[3–12] The heating wire directly contacted the back of the substrate and the annealing temperature was controlled at $\sim$192 °C, as calibrated with an Omegalabel temperature monitor (Omega, Stanford, CT) attached to the bare substrate surface. The samples were moved at a fixed rate of 6, 9, or 12 μm/min. After a single pass, the spin-coated amorphous thin film samples became crystalline as shown in Fig. 1(b), which was obtained between two crossed polarizers with an optical microscope. The annealed films contained many single crystal domains showing different colors that changed upon sample rotation. For example, the green and dark-brown colors shown in Fig. 1(b) changed, respectively, into brown and yellow after the sample was rotated by 34°. The different colors represent different orientations of the single crystals as seen with other compounds.[13] Systematic rotation of the sample revealed that the color change sequence was identical for most single crystal domains, indicating that the different domains were oriented differently only in the direction parallel to the substrate surface.[13] Without the polarizer, however, those different domains were indistinguishable, that was also true for photoluminescent images unless a polarizer was in place. By contrast, the spin-coated amorphous film before annealing appeared dark everywhere between two crossed polarizers. Interestingly, if the same types of spin-coated films were annealed uniformly in an oven at different temperatures (from 170 to 220 °C in 10 °C steps) for about 80 h, the crystals that were produced had dimensions well below 1 μm, while the moving zone annealing produced single crystals in the size range of 100 μm. This result is analogous to laser induced crystallization that gave greater rates of growth on amorphous Si samples than did isothermal heating, which was ascribed to ''the heated zone (being) in compression, which would favor a transition from amorphous to denser crystalline material.'' [14]

Importantly, the optoelectronic properties of the $Ru(bpy)_3(ClO_4)_2$ thin films were dramatically improved after the treatment. As shown in Fig. 2, the intensity of the

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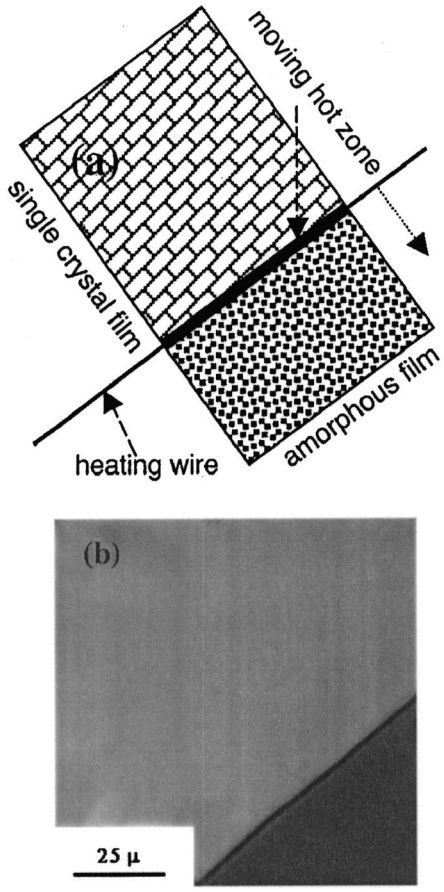

FIG. 1. (a) Schematic diagram of the moving-zone-annealing apparatus. (b) Optical image of single crystalline thin film of $Ru(bpy)_3(ClO_4)_2$ produced from spin-coated amorphous film about 100 nm thick on an ITO substrate by the moving-zone-annealing technique at a rate of 6 μm/min and temperature of 192 °C. Image was taken between two crossed polarizers with an optical microscope. Note that colors shown in the image changed upon sample rotation due to the crystal orientation dependent light absorption. Color version of Fig. 1(b) can be viewed at http://www.cm.utexas.edu/bard/APL%20Figures.html.

photoluminescence was significantly enhanced in the converted single crystalline thin film compared to the unconverted amorphous $Ru(bpy)_3(ClO_4)_2$ film. Note that the spin-coated amorphous film did show clear photoluminescence,[12]

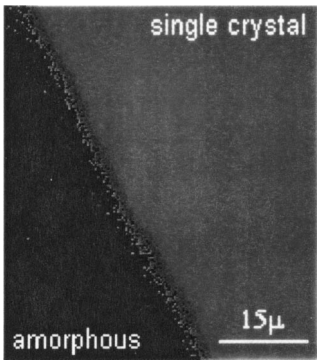

FIG. 2. Photoluminescent image of a $Ru(bpy)_3(ClO_4)_2$ thin film that was initially prepared by spin coating and then partially converted into single crystal by the moving-zone-annealing technique at a rate of 6 μm/min and temperature of 192 °C. Note that the luminescence from the unconverted amorphous film was clearly seen; it appears dark in the image only because the contrast with the luminescence from the crystal area was too large. Color version of figure can be viewed at http://www.cm.utexas.edu/bard/APL%20Figures.html.

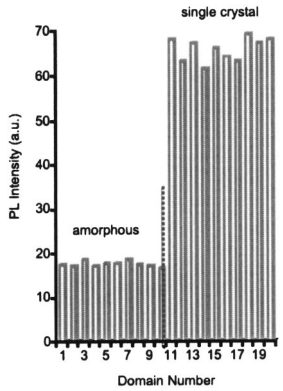

FIG. 3. Emission intensity at different area on a $Ru(bpy)_3(ClO_4)_2$ thin film that was initially prepared by spin coating and then partially converted into single crystal by the moving-zone-annealing technique at a rate of 6 μm/min and temperature of 192 °C.

but it appeared ''dark'' in the image only because its contrast with the crystalline film was too large. Amorphous film in general contains more structure defects that could serve as quench sites leading to a low efficiency in luminescence. Statistics from different areas indicated that the emission intensity varied by about 3.5 times from amorphous to crystalline films as shown in Fig. 3. As expected, improvement was also seen with electroluminescence from LEDs consisting of ITO/$Ru(bpy)_3(ClO_4)_2$/carbon paste or Ga:In alloy. Compared to the unconverted amorphous sample at a given bias, the crystalline films showed higher luminance level and external quantum efficiency up to 3.6%, consistent with early

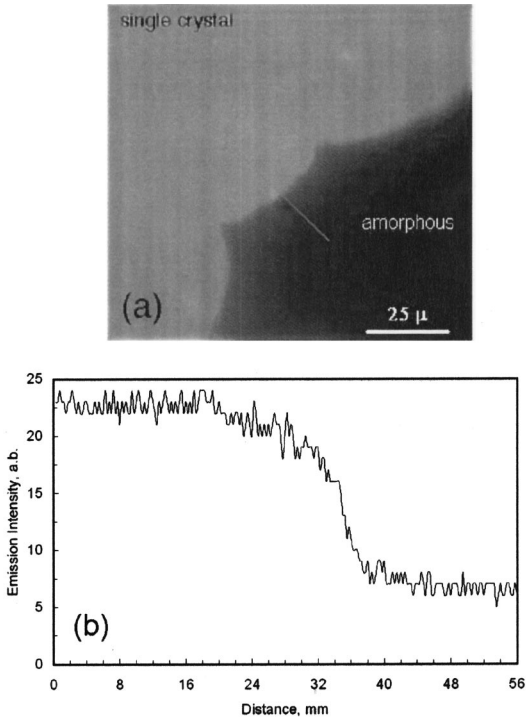

FIG. 4. (a) Luminescent image of an Alq_3 film prepared by vacuum sublimation about 212 nm thick on an ITO substrate; a portion of the film was converted into single crystal at a temperature of 230 °C with the moving-zone-annealing technique. Note that the emission from the amorphous film was easy to see, it appears dark here due to the huge contrast with the crystal area. (b) Emission intensity profile along the line shown in (a). Color version of Fig. 4(a) can be viewed at http://www.cm.utexas.edu/bard/APL%20Figures.html.

studies with amorphous and single crystal $Ru(bpy)_3(ClO_4)_2$.[3–12]

To demonstrate the generality of the moving zone annealing technique, amorphous thin films of 8-hydroxyquinoline, aluminum (Alq_3) about 212 nm thick were prepared through a vacuum sublimation on ITO substrates. At a temperature about 230 °C, the amorphous Alq_3 was successfully converted into crystalline thin films. The uniformly dark appearance of the amorphous films between two crossed polarizers became bright after the conversion as examined with an optical microscopy, indicating the formation of single crystalline thin films. Yellowish-green was the dominate color in the crystalline films of Alq_3 in contrast with the multicolor appearance from $Ru(bpy)_3(ClO_4)_2$ crystalline films (Fig. 1), where the optical absorbance depended on the crystal orientation. As expected, the crystalline films could only be recognized with polarized light. Again, the emission intensity was greatly increased after the conversion as shown in Fig. 4 (top). In most areas, the ratio of photoluminescence from crystalline film over untreated amorphous film was about three times, as shown in the intensity profile (Fig. 4), while in a few spots which appeared significantly brighter, an improvement of about 12–13 times was observed. Similar enhancement was seen in electroluminescence with crystalline Alq_3 based single layer LEDs of ITO/Alq_3/Ga:In, although the efficiency was still below 1% due to an imbalanced charge injection from the two electrodes.

In conclusion, we have demonstrated that moving zone annealing is a simple, low cost, and general technique for the conversion of amorphous organic and inorganic thin films into single crystals. It provides opportunities for producing high luminescent thin films that could find wide applications including optoelectronic devices.

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