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Thermal Diffusivity of Film/Substrate Structures Characterized by Transient Thermal Grating Method *

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Transient thermal grating method is used to measure the thermal diffusivity of absorbing films deposited on transparent substrates. According to periodically modulated dielectric constant variations and thermoelastic deformations of the thin films caused by the transient thermal gratings, an improved optical diffraction theory is presented. In the experiment, the probing laser beam reflectively diffracted by the thermal grating is measured by a photomultiplier at different grating fringe spaces. The thermal diffusivity of the film can be evaluated by fitting the theoretical calculations of diffraction signals to the experimental measured data. The validity of the method is tested by measuring the thermal diffusivities of absorbing ZnO films deposited on glass substrates.

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Characterizations of thermal properties of thin films deposited on substrates are very important for electronic, photoelectronic and microelectronic sciences and technologies. An ideal method for the thin film characterization must be sensitive, rapid and nondestructive during the evaluation processes. Owing to the development of laser technologies, different photothermal methods have become popular for the characterization of thin films deposited on substrates. One of these methods is a transient thermal grating (TTG) method, in which two coherent pulsed laser beams are superposed with each other to produce an interference pattern on the surface of layered sample.[1−4] The laser energy with the interference fringes absorbed by an opaque or absorbing layer of the sample induces a periodic transient thermal gratings in the opaque or absorbing layer by the periodic temperature increase and thermal expansion, which can be observed by reflected diffraction experiments of a probe beam[1,2,4] or by reflected deflection effects of a well-focused probe beam from the corrugation of the deformation grating of opaque materials.[3] The former is always used to characterize thermal diffusivities and the latter is always used to evaluate mechanical or elastic properties of samples. Marshall *et al.*[5] considered theoretically a film of absorbing material on a transparent substrate with periodically modulated dielectric constant in the TTG and measured the time-dependent diffraction light intensities for $Yba_2Cu_3O_{7-x}$ thin films deposited on MgO substrates. Then the thermal diffusivities and other properties of $Yba_2Cu_3O_{7-x}$ thin films were studied. However, Marshall *et al.*[5] have not considered the diffraction effect of the periodical deformation grating induced by the TTG.

In this Letter, an improved theory is presented to calculate the reflected diffraction effects induced by the TTG, in which both the periodic modulations of the dielectric constant and surface deformation of the samples are considered. In the experiment, several optically absorbing ZnO films deposited on glass substrates are taken as the samples. By the theoretical fitting of the experimental results, the thermal diffusivities of the absorbing ZnO films have been obtained, which are very close to that of typical ZnO films obtained by photo-modulated reflectivity method.[6]

For an opaque or absorbing film deposited on a transparent substrate, a TTG is formed on the film by irradiation of two coherent pulsed laser beams superposed with each other on the film surface of the layered sample, as shown in Fig. 1. As the thickness of the film is larger than the optical penetration depths as well as the thermal diffusion lengths of the films, the films can be considered as a semi-infinitive material.[5] For semi-infinite materials, the three-dimensional (3-D) thermal diffusion equation can be expressed as

$$D\nabla^2 T(x,y,z,t) = \frac{\partial T(x,y,z,t)}{\partial t}, \tag{1}$$

with the initial condition

$$T(x,y,z) = \frac{T_0}{2} e^{-\Omega x}\left[1+\cos\left(\frac{2\pi y}{\Lambda}\right)\right] \cdot e^{-(y^2+z^2)/(2a^2)}, \quad (t=0), \tag{2}$$

where D is the thermal diffusivity, T and T_0 are transient and initial temperatures respectively, Λ and Ω are the grating fringe space and the attenuation constant in the film respectively, and a is the radius of the pumping beam.

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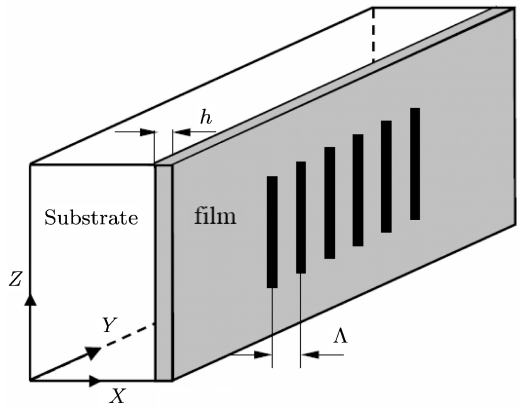

Fig. 1. Transient thermal grating geometry of layer structure.

The 3-D problem can be simplified by separation of variables with the corresponding boundary conditions, i.e., with the adiabatic condition at the surface, and the continuity of heat flow and temperature at the interface of the layered sample.

In the z direction, the thermal profile can be treated as a constant,

$$T(z,t) = 1. \tag{3}$$

In the y direction (grating direction), the sinusoidally modulated dielectric constant leads to a solution[5]

$$T(y,t) = -\frac{1}{2}[1 + e^{-D(2\pi/\Lambda)^2 t}\cos(\Lambda y)]. \tag{4}$$

The diffusion in the x direction is more complicated. The temperature difference ΔT between peak and null of the grating, i.e., in the grating amplitude scale, is

$$\Delta T(x,t) = \frac{T_0}{2} e^{-D(2\pi/\Lambda)^2 t} T(x,t). \tag{5}$$

To calculate the reflected diffraction intensity of the TTG, two effects, i.e., periodically modulated dielectric constant and deformation displacement induced by the TTG in the surface layer of the film, should be considered. Thus the diffraction efficiency $\eta(t)$ of the probing light beam by the TTG can be expressed as

$$\eta(t) = \eta_e(t) + \eta_d(t), \tag{6}$$

where $\eta_e(t)$ and $\eta_d(t)$ are the diffraction efficiencies induced by periodically modulated dielectric constant and deformation displacement, respectively.

First, by considering the periodically modulated dielectric constant, the time-dependent reflected diffraction efficiency $\eta_d(t)$ can be expressed as[5]

$$\eta_e(t) = \frac{k^2\gamma^2(C^2+D^2)}{(1+\eta^2)^4}\Big[\Big|\int_0^h \cos(2knx) \cdot e^{-\Omega x}\Delta T(x,d)dx\Big|^2 + \Big|\int_0^h \sin(2knx)e^{-\Omega x}\Delta T(x,t)dx\Big|^2\Big]. \tag{7}$$

By keeping only the terms affected the time dependence of the diffracted signal, then

$$\eta_e(t) = C_0 e^{-2D(2\pi/\Lambda)^2 t}\Big|\frac{T_0}{2}\int_0^h [a(x)+ib(x)]T(x,t)dx\Big|^2, \tag{8}$$

where $k = 2\pi/\lambda$ with λ being the wavelength of the probe beam; γ, n and h are the effective thermal expansion coefficient, refraction index and thickness of the film; C and D are constants determined by n; C_0 is a proportional constant; $a(x) = \cos(2knx)e^{-\Omega x}$ and $b(x) = \sin(2knx)e^{-\Omega x}$.

Second, considering the deformation induced by TTG, the periodically modulated displacement of the surface can be expressed as[7]

$$U(y,t) = \alpha\frac{1+\sigma}{1-\sigma}e^{-D(2\pi/\Lambda)^2 t}\cos(\Lambda y)\frac{T_0}{2}\int_0^h T(x,t)dx, \tag{9}$$

where α is the linear thermal expansion coefficient of the film, σ is Poisson's factor. If $U_0(t) = \alpha\frac{1+\sigma}{1-\sigma}e^{-D(2\pi/\Lambda)^2 t}\frac{T_0}{2}\int_0^h T(x,t)dx$, then

$$U(y,t) = U_0(t)\cos\Lambda y). \tag{10}$$

Generally $U_0(t)$ is very small, the first order diffraction intensity can be simplified to $I_1 = I_0(2\pi U_0/\lambda)^2$. The diffraction efficiency $\eta_d(t)$ can be then expressed as

$$\eta_d(t) = \Big(\frac{T_0}{2}\frac{2\pi\alpha}{\lambda}\frac{1+\sigma}{1-\sigma}\Big)^2 \cdot e^{-2D(2\pi/\Lambda)^2 t}\Big(\int_0^h T(x,t)dx\Big)^2. \tag{11}$$

Finally, the diffraction efficiency is

$$\eta(t) = e^{-2D(2\pi/\Lambda)^2 t}\Big\{C_0\Big|\frac{T_0}{2}\int_0^h [a(x) + ib(x)]T(x,t)dx\Big|^2 + \Big[\frac{T_0}{2}\frac{2\pi\alpha}{\lambda}\frac{1+\sigma}{1-\sigma}\int_0^h T(x,t)dx\Big]^2\Big\}. \tag{12}$$

Therefore, as the reflected diffraction signals are detected, the thermal diffusion of the films can be calculated from Eq. (12).

Figure 2 schematically shows the experimental setup.[4] A frequency doubled pulsed Nd:YAG laser (532 nm, 8 ns) is used as the pumping source. The pumping laser beam is split into two beams with the equal intensity and the same polarization. Both

beams are reflected separately and then superposed with an angle of 2θ from each other on the surface of a bilayered sample to produce a time-dependent interference pattern. Then periodically modulated dielectric constant and surface displacement are generated by the thermal grating induced by the interference pattern, in which the period Λ of the grating is determined by the angle 2θ. A He-Ne laser beam incident on the grating of the surface is used as the probing beam. The reflected one-order diffraction beam is detected by a photomultiplier and the output is recorded by a digital oscilloscope for further analysis. The resulted time-dependent diffraction signal reflects the time-dependent decay of the dielectric constant and the deformation modulations induced by the TTG.

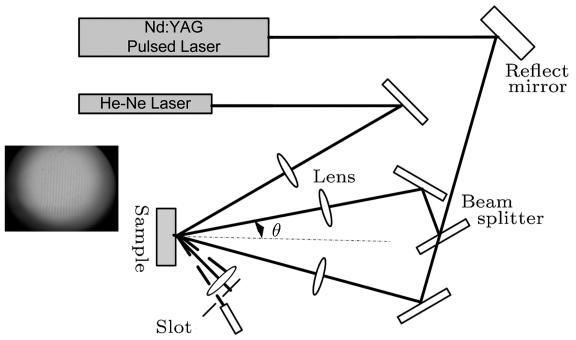

Fig. 2. Experimental setup.

If the grating fringe space, Λ is changed as Λ', the reflected diffraction efficiency becomes as $\eta'(t)$, then dividing one diffraction efficiency by the other yields

$$\frac{\eta(t)}{\eta'(t)} = \exp\Big[-8D\pi^2 t\Big[\frac{1}{\Lambda^2} - \frac{1}{\Lambda'^2}\Big]\Big]. \qquad (13)$$

Finally, from the variations of the reflected diffraction efficiencies in both grating fringe spaces, the thermal diffusivity D of the film can be obtained without any prior knowledge on the material of the sample.

Several ZnO films with different thicknesses of 4.25, 4.32 and 4.35 μm deposited on glass substrates with thickness 1 mm have been used as the samples, as listed in Table 1. It is well known that the ZnO films are always transparent, whereas in this case the ZnO films display a grey colour due to the deposition under the condition of insufficient ratio of oxygen to argon.

Table 1. Parameters of the ZnO film. Here the thickness of the sample is measured by a step profiler with the precision 10 nm.

Sample	1	2	3
Thickness (μm)	4.25	4.32	4.35
Thermal diffusivity (cm^2s^{-1})	7.51×10^{-2}	8.15×10^{-2}	8.32×10^{-2}

In order to characterize the crystal structure and chemical state of the ZnO films, x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) patterns and scanning electronic microscopic (SEM) images have been obtained. The XRD patterns of the samples display only one strong peak at $2\theta = 34.43°$, as shown in Fig. 3, which means that the film has a strong c-axis (002) texture and in isotropy at the Y–Z plane.

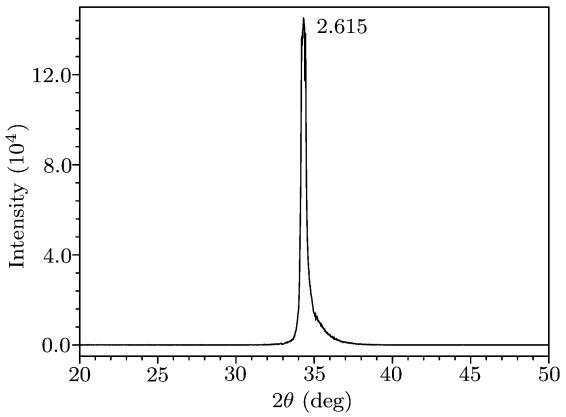

Fig. 3. XRD spectrum of the ZnO film deposited on a glass substrate.

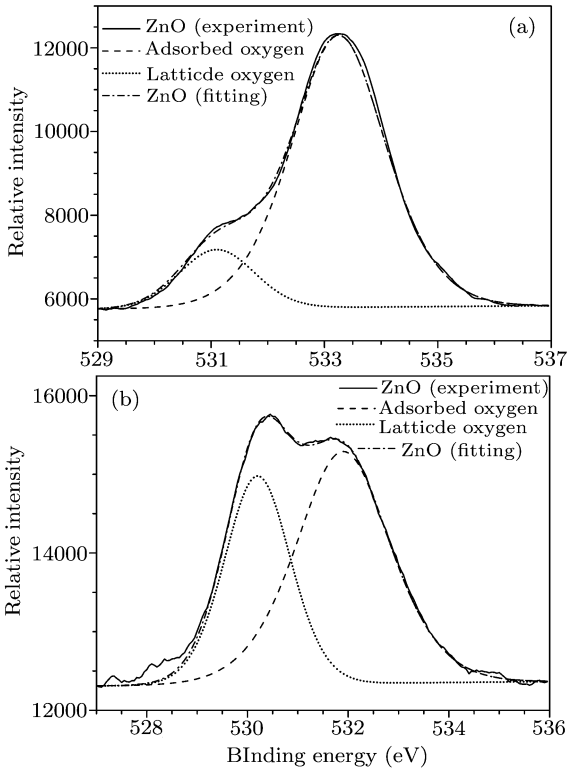

Fig. 4. XPS pattern of O 1s spectra of ZnO film: (a) oxygen deficiency state, (b) normal.

However, the XPS patterns of the samples show quite different situations from those of typical ZnO films. As an example, the XPS pattern of the O 1s spectrum of sample 1 is shown in Fig. 4(a), in which

the core peak at the binding energy 533.2 eV is attributed to the chemisorbed oxygen. Compared with the O 1 s spectrum of a typical ZnO film shown in Fig. 4(b), in which the binding energy of ZnO structure is 530.2 eV,[8] it may be concluded that a large chemisorbed oxygen in the ZnO structure of sample 1 makes the binding energy shift to higher energies.[9] The result also demonstrates that the ZnO films are in oxygen deficiency state, which may induce the grey colour of the films.

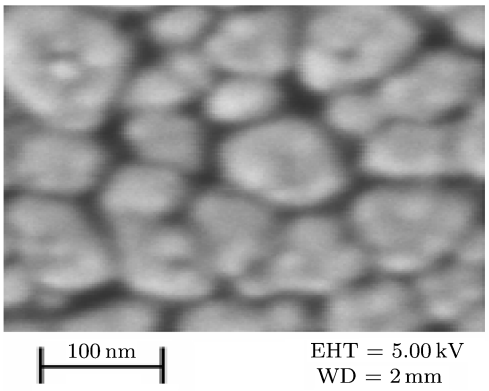

Fig. 5. SEM micrograph of the ZnO film deposited on a glass substrate.

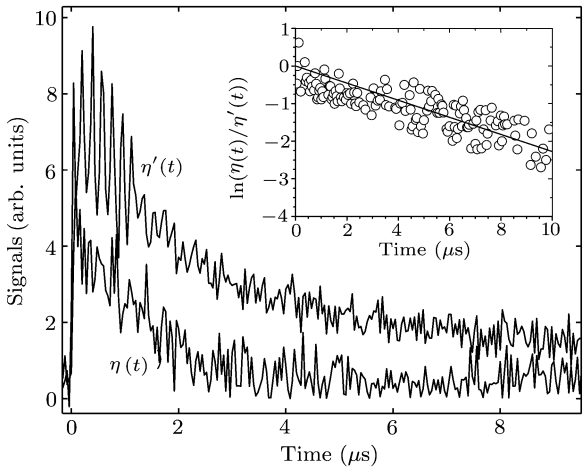

Fig. 6. Detected diffraction signals at different fringe spaces. Inset: fitted results. Circle: experimental data. Solid line: theoretical fitting.

The SEM image of ZnO film for sample 1 is presented in Fig. 5, which shows that the ZnO film consists of nanoscaled crystal grains. The grain size is not homogeneous, and the measured properties of the films could be altered by optical dispersion effects.

The detected diffraction signals of sample 2 at the different grating fringe spaces of 69.4 μm (large) and 41.5 μm (small) are shown in Fig. 6. According to Eq. (13), using the least squares algorithm to fit the peak and exponential decay of the theoretical curve of $\eta(t)/\eta'(t)$ to the experimental data, the thermal diffusivity of the film can be directly deduced without any prior knowledge. Based on the repetitive measurements, the repetition of the experimental results is about $\pm 5\%$ and the thermal diffusivities of the ZnO films deposited on glass substrates are presented in Table 1.

The thermal diffusivities of three samples are different from each other, which may be caused by the deposition conditions, such as the surface roughness of the films is different from the result determined by the step profiler,[9] and the measurement errors, such as the ratio of diffraction signal to noise is not very good. However, the average of the thermal diffusivities of three ZnO films is $D = 7.99 \times 10^{-2}\,\mathrm{cm^2 s^{-1}}$, which approaches the thermal diffusivity of $D = 8.17 \times 10^{-2}\mathrm{cm^2 s^{-1}}$ of ZnO films obtained by the traditional method.[6]

In summary, a TTG method is used to characterize the thermal diffusivity of absorbing films (ZnO) deposited on transparent substrates (glass). Firstly, an improved diffraction theory of TTG is presented. Then the thermal diffusivities of absorbing ZnO films grown in the c direction have been obtained. These results demonstrate that the TTG method is a useful technique to evaluate thermal properties of the films deposited on substrates, especially for opaque films deposited on transparent substrates.

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