New Thermoelectric Materials and New Applications

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Abstract: Thermoelectricity in general is of strong scientific and technological interest due to its application possibilities ranging from clean energy to photo sensing devices. Recent development in theoretical studies on the thermoelectric effects, as well as the newly discovered thermoelectric materials provide new opportunities for wide applications. One type of these materials is based on the strongly correlated electron systems; typical examples are the transition metal oxides, which were not regarded as very promising for thermoelectric applications. A discussion is made on some recent progress in this field, and special emphasis is laid on the new application of thin films grown on vicinal cut substrates. The thermoelectric effect is based on the anisotropic Seebeck components in crystals. Upon radiation of heat and/or light on the film surface, there will be an induced voltage; hence a device which can detect the heat and/or light radiation can be made. It is pointed out that this type of detector demonstrates novel properties: broad optical response, very fast response and at the same time it does not need any bias, therefore it is extremely energy saving. The performances of three typical compounds $YBa_2Cu_3O_{7-\delta}$, $LaCaMnO_3$ and $LaSrCoO_3$ are presented.

Key words: Anisotropic Seebeck effect; laser - induced thermoelectric voltage; thermoelectric materials

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新型热电材料及其新应用

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摘要: 热电材料,由于在清洁能源、光电子探测等诸多方面有巨大的应用前景,因而受到科学上和技术上的广泛关注.最新的理论进展和若干新材料的发现,为人们提供了新的应用机会.一类新材料就是基于强关联电子系统,典型例子是过渡族金属氧化物,这类材料以前从热电材料的角度并未受到重视.我们将讨论几点最近的进展,着重讨论生长在倾斜切割衬底上薄膜的新的应用.这种情况下热电电压的产生是基于各向异性的塞贝克效应.当光辐射照射到薄膜表面时,薄膜上下表面的温差引起横向的电势差,从而可用于光、热辐射的探测.我们论证:这类探测器有很具特色的优点,宽的光谱响应,快的时间响应,同时不须施加偏压或偏流,因而十分节能.我们还讨论了几种典型材料的性能.

关键词: 各向异性塞贝克效应;激光感生电压;热电材料

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1 Introduction

Thermoelectrisity was discovered in 1821, and has been interesting from the point of view of basic science since then. After about 100 years of efforts it was found that the effect can be applied to refrigeration and power generation in very special cases in 1950 s. There were great efforts to explore more effective materials, especially among the semiconductors[1~4]. The theory predicted at that time that the figure of merit for thermoelectric application is $Z = S^2/\kappa\rho$, with S being the Seebeck coefficient, κ the thermoconductivity and ρ the resistivity. A large S, low ρ and low κ should be found in semiconducting materials with carrier density of about $10^{19}/cm^3$. Recently, due to the discovery of high T_c superconductor, new group materials have been studied widely and deeply. These are the strongly correlated transition metal oxides, which demonstrate novel properties not only in superconductivity but also in magnetic, thermoelectric and other related properties. The progress in theory of transport properties in these transition metal oxides predicts at the same time new direction for searching new thermoelectric materials[5~9]. On the other hand, the new discovery of a laser induced thermoelectric voltage effect (LITV) in $YBa_2Cu_3O_{7-\delta}$(YBCO)[10~13] and colossal magneto resistance (CMR) materials such as $LaCaMnO_3$(LCMO) thin films[14~16] has trigged new interests in the study and application of thermoelectrisity, since this new effect was proved to be based on the off - diagonal components of the Seebeck tensor in single crystals. The principle and application are very different from the early concepts.

In this paper, we report recent progress in the study of new thermoelectric materials and their new applications. Special emphase is on the single crystal and single crystal type thin film materials, which posses anisotropic Seebeck tensor components.

The equations to describe the flow of electric and heat currents in an anisotropic solid are[17]:

$$j_i^e = -\alpha_{ik}\frac{\partial\bar{\mu}}{\partial x_k} - \beta_{ik}\frac{1}{T}\frac{\partial T}{\partial x_k} \tag{1}$$

$$h_i = -\beta_{ki}\frac{\partial\bar{\mu}}{\partial x_k} - \gamma_{ik}\frac{1}{T}\frac{\partial T}{\partial x_k} \tag{2}$$

where j_i^e and h_i are the electric current and the heat flow density respectively, and , $\bar{\mu} = \mu - e\Phi$, with Φ and μ are the electrical and chemical potential. The coefficients α_{ik}, β_{ik}, β_{ki}, γ_{ik} are tensors for case of single crystals. The thermoelectric potential is produced and expressed as along certain direction in unitary length, when there is no electric current:

$$-\frac{\partial\Phi}{\partial x_i} = -\frac{1}{e}\left(\varepsilon_{ik}\frac{\partial T}{\partial x_k} + \frac{\partial\mu}{\partial x_i}\right) \tag{3}$$

where e is electron charge

$$\varepsilon_{ik} \equiv \alpha_{ik}^{-1}\beta_{ik}\frac{1}{T} \tag{4}$$

is Seebeck tensor (or thermoelectric tensor). It is easy to prove that $\alpha_{ik} = \sigma_{ik}/e^2$, where $\sigma_{ik}$is the electrical conductivity tensor of the crystal. For homogenous media $\partial\mu/\partial x_i = 0$, then

$$\frac{\partial\Phi}{\partial x_i} = \frac{1}{e}\varepsilon_{ik}\frac{\partial T}{\partial x_k} \tag{5}$$

and this means that the direction of temperature gradient is not necessary to coincide with that of potential gradient due to the tensors feature of a crystal. The expression of Seebeck tensor varies according to the crystal symmetries.

$YBa_2Cu_3O_{7-\delta}$ crystal is of orthorhombic structure, and its Seebeck tensor is

$$\begin{pmatrix} S_{xx} & 0 & 0 \\ 0 & S_{yy} & 0 \\ 0 & 0 & S_{zz} \end{pmatrix} \tag{6}$$

For YBCO, $S_{xx} = S_{yy} = S_{ab}$, and S_{ab} is the Seebeck coefficient in CuO_2 plane, it is different from the c - axis component $S_c = S_{zz}$. For an YBCO thin film grown on vicinal cut substrate the normal of the thin film surface (z)

is not coincided with the main axis c of the crystal, and there is an angle α between them (Fig.1) is given by the angle of the vicinal cut. Under this condition, Seebeck tensor(6) is transformed to

$$\begin{pmatrix} S_{11} & 0 & S_{23} \\ 0 & S_{22} & 0 \\ S_{31} & 0 & S_{33} \end{pmatrix}, \tag{7}$$

where $S_{33} = S_{11} = S_{ab}\sin^2\alpha + S_c\cos^2\alpha$, and $S_{22} = S_{ab}$ and $S_{31} = S_{13} = \frac{1}{2}\sin(2\alpha)(S_{ab} - S_c)$.

When the surface of the thin film absorbs a radiation, a temperature difference ΔT_z along z direction is generated, and $\Delta T_x = \Delta T_y = 0$, if the film is heated from top homogeneously. Supposing that the thickness of the thin film is d, and the temperature distribution is homogeneous along z direction, the temperature in the thin film is $(\partial T/\partial z) = (\Delta T_z/d)$. Substituting the tensor components of Seebeck tensor(7) into Eq. (5), one obtains

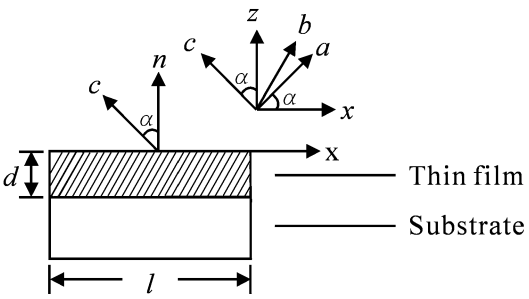

Fig.1 A YBCO or LCMO thin film grown on a vicinal cut substrate and the coordinate systems

$$\frac{\partial \Phi}{\partial x} = \frac{1}{2}\sin(2\alpha)(S_{ab} - S_c)\frac{\Delta T_z}{d} \tag{8}$$

$$\frac{\partial \Phi}{\partial y} = 0 \tag{9}$$

$$\frac{\partial \Phi}{\partial z} = (S_{ab}\sin^2\alpha + S_c\cos^2\alpha)\frac{\Delta T_z}{d} \tag{10}$$

Therefore the temperature difference ΔT_z induced by laser radiation can generate not only the potential along z direction but also the potential along x direction. The integration of Eq.(8) along x direction and Eq. (10) along z direction leads to

$$V_x = \int_0^l \frac{\partial \Phi}{\partial x}\mathrm{d}x = \frac{1}{2}\frac{\Delta T_z}{d}(S_{ab} - S_c)\sin(2\alpha) \tag{11}$$

$$V_z = \int_0^d \frac{\partial \Phi}{\partial x}\mathrm{d}z = \Delta T_z(S_{ab}\sin^2\alpha + S_c\cos^2\alpha) \tag{12}$$

Eq. (11) and Eq. (12) show that the transverse thermoelectric potential V_x and vertical thermoelectric potential V_z are directly proportional to the temperature difference ΔT_z and depend on the tensor components. Especially V_x is directly proportional to $(S_{ab} - S_c)$ and increases with α. Eq. (11) can explain many phenomena[18], however it failed in explaining the relation between V_x and the film thickness d. In fact, V_x can not be increased with $1/d$ as d goes to zero. Furthermore, Eq. (11) supposes that ΔT_z is a constant, and does not vary with time, hence it is difficult to discuss the time dependent LITV signals.

2 Designing fast response detector based on LITV

Using a micro - cell network model, based on the atomic layer thermopile model, we deduced a formula which describes the time - dependence of LITV. The formula is[19]

$$U(t) = \frac{\alpha_0 El\sin(2\alpha)}{4d\rho c_0\sqrt{\pi Dt}}(S_{ab} - S_c)(e^{-\frac{\delta^2}{4Dt}} - e^{-\frac{d^2}{4Dt}}) \tag{13}$$

where E is the laser energy density per pulse, α_0 is the laser absorption coefficient, ρ is the mass density, c_0 is the specific heat, δ is the laser penetration depth, and D is the thermal diffusion constant of the thin film. Eq. (13) describes the time evolution of the induced signals and explains the measured result between the peak voltage and the film thickness d in YBCO thin films[3].

We can see from Eq. (13) that LITV signal at any time t is directly proportional to α_0、E、$\sin(2\alpha)$ 、l and

$S_{ab} - S_c$, and inversely related with ρ and c_0. We now discuss the influence of parameters δ, D, and d on LITV signals. With the increasing of penetration depth δ, the peak value of LITV U_p decreases, and the time constant τ increases monotonously. δ is related to the character of thin film and the wavelength of the incident laser. In practical applications, in order to obtain a device with higher U_p and smaller τ, that is with higher sensitivity and fast response, one can select materials with smaller δ at the used wavelength, or take measure to spread another material on top of the thin films, which is with small δ.

With decreasing the thermal diffusion constant D, the τ increases and U_p shifts to large value in time. This is easy to understand because D embodied the diffusion speed of heat, so the higher D, the faster the thermal equilibrium is reached, hence a smaller τ is reached.

It can be shown that there exists an optimum thin film thickness d in order to obtain largest peak voltage U_p. Small d can decrease the time constant τ but reduce the peak intensity, while large d will reduce the peak intensity as well increase the time constant, hence is more harmful to the performance of the device.

It should be mentioned that the time response of these thin films to pulsed laser is very fast. The voltage is produced in an atomic layer thermopile, as long as there is a temperature gradient generated by what means, there is a voltage produced, and the carriers move only a very short distance, a scale of the lattice parameter. This is different from the traditional thermal devices, say bolometers, which function with long time constant, because to reach thermal equilibrium needs more time. In LCMO thin films the rising time (for the signal rising from 0 to the peak) of LITV can reach ns order, and in YBCO thin films, can reach ps order[20].

This type of detector does not need any electric bias like traditional semiconductor or bolometers, since they are based on the principle of atomic layer thermopile. Therefore it is extremely energy saving.

3 Conclusion

In conclusion, laser induced thermoelectric voltage (LITV) effect had been found in YBCO, LCMO and $LaSrCoO_3$ thin films, and this effect is originated from the anisotropic Seebeck effect in the crystals. This is an intrinsic property of crystals; hence many other crystals may demonstrate the effect. Due to the different properties, these crystals can be used for different purpose or at different wavelengths. According to the time dependent LITV relation one can design light or heat detectors working in wide spectrum range with fast response. To obtain a detector with fast response, the thermal diffusion constant D of the thin films must be big. Moreover, to obtain the optimum performance of the thin film the penetration depth δ under the working wavelength must be as small as possible, and the optimum thin film thickness d must be reached.

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