Plasma Model for Energy Transformation Mechanism of Non-Thermal Microwave Effect

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Microwaves generate ordered motion in material structures. Microwaves can transfer energy while maintaining coherency; this is the origin of the microwave effect. We suggest that the non-thermal energy path during microwave heating really exists and that a plasma model can explain the non-thermal enhanced-reduction in microwave heating.

Keywords: microwave effect, non-thermal reduction, Landau damping, coherent phonon

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Since 1990's the unpredictable behaviors of materials under microwave irradiation (microwave effect) have received considerable attention in the field of microwave processing. Nitridation of metals in air and un-expected phase transitions of crystals were reported as examples of the microwave effect [1–3]. These reports are based on phenomenological descriptions and the physical and chemical mechanism of the non-thermal microwave effects has not been studied yet by organized experimental and theoretical study. In this study, microwave effects were clearly revealed, and the energy path during microwave heating was estimated using a plasma model.

The reduction speed of CuO was studied in high vacuum. Figure 1 (a) shows a schematic view of the experimental system. The reduction speeds at each temperature were measured by analyzing the partial pressure of out-gas from the heated sample using a quadrupole mass analyzer in high vacuum. The sample temperature was measured by an infrared radiation thermometer. Cylindrically packed CuO powder (ϕ 8 mm $\times$ 2 mm) was placed in the TE103 cavity tuned to 2.45 GHz. The sample was small enough not to disturb the electromagnetic field distribution in the cavity. The sample was heated at the maximum point of the H-field in the cavity or in a conventional infrared furnace.

The experimental results are shown in Fig. 1 (b). The temperature at which reduction starts is low under H-field irradiation. Moreover, the reduction speed in the H-field was at least one-order faster than that in conventional heating. Therefore, the reduction reaction was obviously enhanced when the sample was subjected to the H-field compared with the effect under conventional heating. The inclination of the plot indicates the apparent activation energy (ΔE). ΔE under conventional heating (ΔE_{conv}) was 333 kJ/mol, and that under H-field heating ($\Delta E_{\text{H-field}}$) was 117 kJ/mol. The rate-controlling reaction is 4CuO $\rightarrow$ $2Cu_2O$ + O_2 [4]. In this reaction, the enthalpy change of formation (ΔH) is 292 kJ/mol. ΔE_{conv} is larger than ΔH; however, $\Delta E_{\text{H-field}}$ is smaller than ΔH. The results suggest that a different energy path unlike that of thermal energy exists to satisfy the reduction energy. This is the first experimental observation of the non-thermal path which the microwave effect originates.

Here we discuss the non-thermal energy path in microwave heating. Microwaves interact with electric charge of materials. Using Maxwell's equations and the Euler equations, the wave equation is solved. The dispersion relations are determined by solving the determinant of the tensor relative dielectric constant [5]. Ordered motion that satisfies a dispersion relations is excited in the material (plasma model).

First, the interaction between microwaves and materials is examined. Materials are inhomogeneous in nature, *e.g.*, clusters or powders of the order of microns, and defects, magnetic domains, and grain boundaries in the submicron range. These distance ranges is defined as meso-scale in this article, namely, 0.1 $\sim$ 100 µm. The wavelengths of mm to cm in free space in the GHz-band are much longer than the meso-scale. When microwaves are irradiated into inhomogeneous materials, the waves are scattered by discontinuities. Mathematically, this can be explained by Fourier expansion.

Next, the Fourier-expanded microwaves excite a collective motion in the materials. When the Fourier-expanded microwaves are irradiated to the lattice, an ordered motion of the electrons is excited. The ordered motion propagates to the atoms, which move collectively to remain in phase with each order. These atomic motions are called coherent phonons. The frequency and phase velocity of the coherent phonons are 2.45 GHz and 10^3 m/s, respectively. Moreover, the atomic motion in the random

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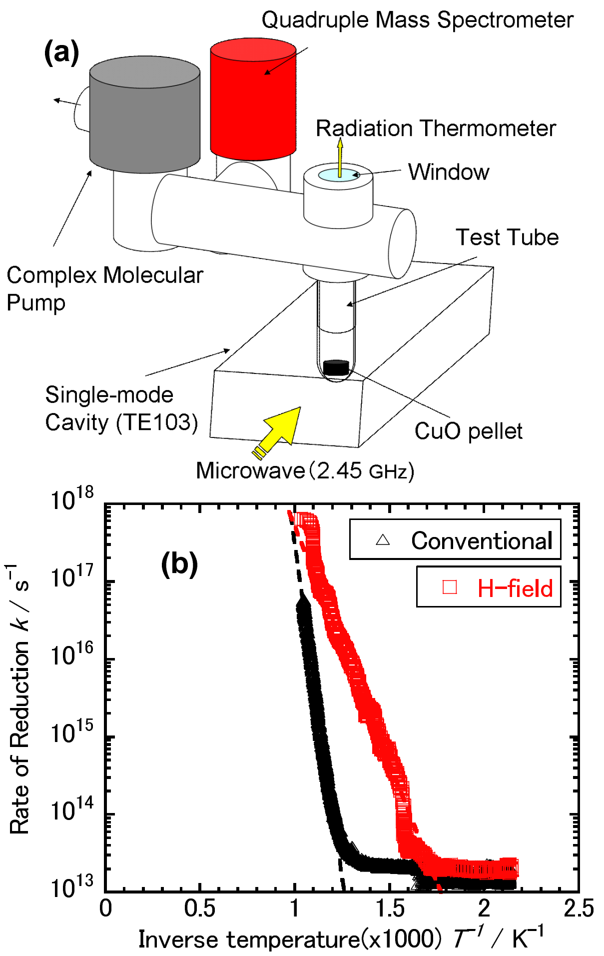

Fig. 1 Schematic view of experimental device and results. (a) Schematic view of experimental device in microwave heating. Air in the system is evacuated continuously by a turbo-molecular pump at 50 l/s. (b) Arrhenius plot of the results. Black triangles indicate the results for conventional heating, red squares indicate those for H-field heating.

phase is called a thermal phonon. The thermal velocity of the lattice is of the order of $\omega_{th}\Delta x$, where, ω_{th} and Δx are the average thermal frequency and length of the thermal motions of ions in the lattices, respectively. At 913 K, ω_{th} is around 50 THz; if we assume that the Δx is 1/10 of the spacing of the lattice ions, or about 100 pm, $\omega_{th} \times \Delta x = 50 \times 10^{12} \times 100 \times 10^{-12} = 5000$ m/s. The thermal velocity is distributed over a wide range. Landau damping can occur in the energy transfer from coherent phonons to thermal phonons in the material. Because Landau damping is a collisionless process, the collective motions in the solid plasma conserve the coherency of the external waves. This produces a higher energy tail in the velocity space, as shown in Fig. 2. The non-equilibrium thermal energy could be the origin of the non-thermal microwave effect.

The distribution of the thermal phonons is expressed by the Debye model [6]. The energy density of Planck's radiation $u(f,T)$ [J/(cm^3 × Hz)] is expressed as follows.

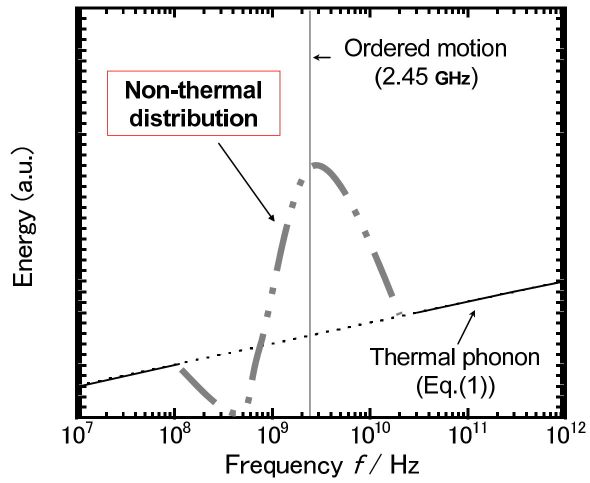

Fig. 2 Schematic view of the relaxation process of coherent phonons. The distribution of thermal phonons obeys the Bose-Einstein distribution.

$$u(f,T) \propto \frac{\pi h f^3}{v^3} \frac{1}{\exp(\frac{hf}{k_B T}) - 1}, \qquad (1)$$

where f, T, h, v and k_B are the frequency, temperature, Planck constant, sound velocity, and Boltzmann constant, respectively. An external force such as electromagnetic waves causes fluctuations in the energy distribution function of thermal phonons. According to the law of entropy growth, the fluctuations are stabilized to the Bose-Einstein distribution in a certain period of time (thermalization). If the external force supplies energy to the fluctuations at a rate much faster than the speed of relaxation to thermal equilibrium, the fluctuations produce a non-thermal distribution of the thermal phonons, as shown in Fig. 2. The gray-dash-dotted line shows a schematic view of the non-thermal distribution. Non-thermal effects like enhanced reduction may occur as the result of the transformation of the energy of the non-thermal distribution into the material's energy, such as the reduction energy.

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