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Subsurface imaging of grain microstructure using picosecond ultrasonics

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ABSTRACT

We report on imaging subsurface grain microstructure using picosecond ultrasonics. This approach relies on elastic anisotropy of crystalline materials where ultrasonic velocity depends on propagation direction relative to the crystal axes. Picosecond duration ultrasonic pulses are generated and detected using ultrashort light pulses. In materials that are transparent or semitransparent to the probe wavelength, the probe monitors gigahertz frequency Brillouin oscillations. The frequency of these oscillations is related to the ultrasonic velocity and the optical index of refraction. Ultrasonic waves propagating across a grain boundary experience a change in velocity due to a change in crystallographic orientation relative to the ultrasonic propagation direction. This change in velocity is manifested as a change in the Brillouin oscillation frequency. Using the ultrasonic propagation velocity, the depth of the interface can be determined from the location in time of the transition in oscillation frequency. A subsurface image of the grain boundary is obtained by scanning the beam along the surface. We demonstrate this subsurface imaging capability using a polycrystalline UO_2 sample. Cross section liftout analysis of the grain boundary using electron microscopy was used to verify our imaging results.

1. Introduction

Grain boundaries serve an important role in defining the physical properties of ceramic materials used in the energy industry [1]. For example, ion transport in solid oxide fuels is affected by atomic segregation at grain boundaries [2]. Grain boundaries can also significantly impact thermal transport in materials used for thermal management as well as high burnup nuclear fuels [3–6]. In addition mechanical properties of energy materials are often influenced by the diffusion of atoms in high stress and high temperature environments [7,8]. Grain boundaries, under these extreme conditions can act as barriers or provide a pathway for atomic diffusion [9,10]. Many of the above mentioned phenomena are strongly influenced by the local environment around grain boundaries [11].

A central complexity in understanding these fundamental mechanisms is that grain boundary character evolves with time. In this regard, grain boundaries attract impurities and other defects that have further implications on determining material behavior [12]. Additionally the boundaries themselves undergo motion under external stimuli such as mechanical deformation, radiation and high temperatures [7,13]. Grain boundary motion and the associated change in crystal misorientation across the boundary can significantly influence transport and mechanical properties [14,15]. To better understand the evolution of boundary structure under external stimuli, there is a need for new experimental techniques that can be used to investigate them nondestructively [16].

Currently the majority of grain boundary evolution studies have been limited to imaging the boundary line on the surface [17,18]. For these investigations, typically a bicrystal is subjected to

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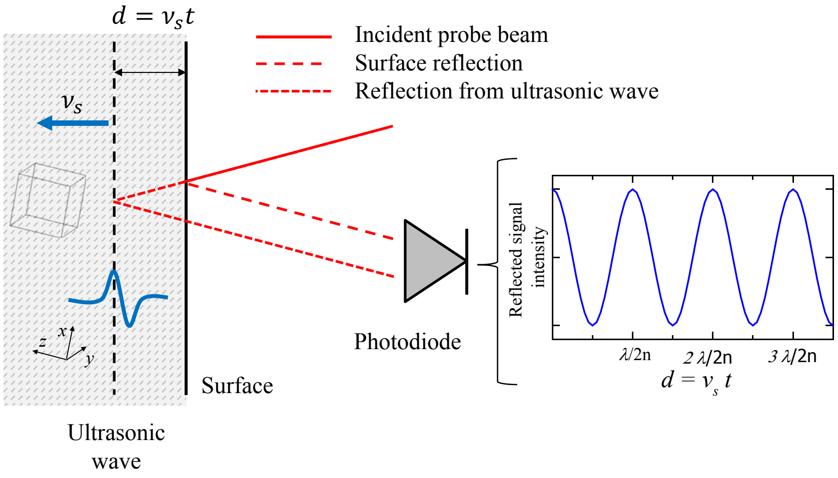

Fig. 1. Schematics of experimental approach used for observation of Brillouin oscillations. Ultrasonic wave excited by a thermoelastic deformation caused by the pump beam and propagating normal to the surface with velocity v_s is represented by a dashed line. Two reflections of the probe beam one from the surface (solid vertical line) and one from the front of ultrasonic wave (dashed vertical line) result in an interference pattern whose period and frequency is proportional to ultrasonic velocity and index of refraction of probe beam in the material. This interference pattern is observed in time resolved reflectivity change of the probe beam. In the actual experiment, the probe is at normal incidence to the surface, here it is shown at angle to emphasize two reflections. Cartesian coordinate system used to calculate the velocity based on ultrasonic wave equation is defined with respect to the grain's crystallographic orientation.

deformation and the motion of the boundary on the free surface is visualized using scanning electron microscopy (SEM). This observation mode can be influenced by surface effects and may not accurately represent the behavior of the boundary in the bulk. Thus availability of techniques providing three-dimensional (3D) structural information is important for understanding bulk behavior. Methods based on advanced X-ray synchrotron sources are able to provide volumetric grain microstructure [19,20]. However, limited availability of synchrotron sources prevents wide spread application of X-ray approaches. A focused ion beam instrument combined with electron backscattering diffraction can be used to obtain a 3D image of the grain boundary structure. This approach involves reconstruction of the 3D structure from a series of 2D crystallographic orientation images obtained after repetitive removal of thin layers using focused ion beam milling [21–23]. Destructive serial sectioning makes this approach not suitable for in-situ measurements. Recently it has been shown that grain inclination with respect to the free surface can be extracted from analysis of the diffraction pattern obtained from the area above the grain boundary. However, the depth resolution of this approach is limited to the penetration depth of electrons [24].

Here we report on an alternative approach, based on picosecond ultrasonics, which is used to visualize depth resolved grain microstructure. This approach has been used previously for depth profiling of elastic inhomogeneities in transparent materials [25,26]. The emphasis here is on mapping the location of a grain boundary below the surface by monitoring changes in ultrasonic velocity caused by a change in crystallographic orientation. We demonstrate this approach using uranium dioxide (UO_2), an important energy material broadly used in the nuclear energy industry as well as having promising applications in the solar energy industry [27,28].

2. Picosecond ultrasonics and Brillouin oscillations

For our application picosecond duration ultrasonic pulses propagating normal to the surface are generated by irradiating UO_2 sample with an ultrashort laser pulse (pump) having above bandgap photon energy. Both thermal expansion and deformation potential mechanisms are responsible for ultrasonic generation. Strong optical absorption ensures generation of short duration ultrasonic pulses [29]. A time delayed probe pulse tuned to a photon energy that is below the bandgap is used to detect the ultrasonic pulses as they propagate into the sample [30]. In materials that are transparent or semitransparent to the probe wavelength, the probe monitors GHz Brillouin oscillations. The origin of these oscillations comes from interference between two components of the reflected probe pulse as illustrated in Fig. 1. The first is from the reflection off the free surface of the sample and the second is due to photoelastic coupling with the propagating ultrasonic wave. The frequency of the oscillations (f) depends on the probe wavelength (λ), the index of refraction at the probe wavelength (n) and the ultrasonic velocity in a direction normal to the surface (v) [30]:

$$f = \frac{2nv}{\lambda}. \tag{1}$$

Detection sensitivity is based on the photoelastic effect, where the strain associated with the acoustic wave modifies dielectric properties. It is known that photoelastic coupling is especially pronounced when the energy of the probe is comparable to the semiconducting gap of the material. The bandgap of UO_2 is ~2.2 eV [36]. Accordingly we tune our probe and pump photon energies to be 1.5 eV (800 nm) and 3 eV (400 nm) respectively. For this combination, the pump is strongly absorbed by the sample and the probe beam is able to penetrate into the sample several tens of microns [38]. A similar approach has been extensively used to observe Brillouin oscillations in GaAs and was implemented to characterize defects in ion irradiated GaAs [31].

The emphasis here is to utilize elastic anisotropy to image subsurface grain microstructure. UO_2 exhibits moderate elastic anisotropy which makes it a good system for demonstration of volumetric imaging of grain boundary structure. In an elastically anisotropic material, the velocity of ultrasonic wave depends on the direction of propagation with respect to its crystallographic axes [39]. As a result, the frequency of Brillouin oscillations depends on the grain orientation. The maximum depth resolution of this approach, using our simple 1D analysis, is related to acoustic diffraction and ultimately limited by optical absorption of the probe beam. In the very near field of the acoustic source, acoustic diffraction can safely be neglected [40]. This region is defined by the lateral dimensions of the source and for the case considered here