Direct observation of the path of ultrasound wave propagation in AgCl crystals by the "print-out effect"

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The effect of ultrasound waves on the "print-out effect" in AgCl cystals was studied at room temperature. When a longitudinal stationary ultrasound wave existed in crystals subjected to electric field and light pulses, black planes caused by the print-out effect were produced. These planes were located perpendicular to the direction of the wave propagation. The distance between the darkened planes roughly equaled a half-wavelength of the ultrasound. They were arranged in nodal planes. It is concluded that these planes are the result of a print-out effect due to fresh dislocation moved by the shear stress of stationary longitudinal waves. The trace of the ultrasound wave propagation was directly observed by the darkening, which is the first direct observation of the wave propagation trace in solids. The effect of a traveling wave on the print-out effect was not observed.

I. INTRODUCTION

It has been observed that if a photographic emulsion containing silver-halide crystals is exposed to strong light for a long time, it becomes dark. Microscopic examination of small single crystals of salt in the emulsion reveals that the darkening is localized in the form of a number of small specks within the grain. Further research has shown that these specks are colloidal metallic silver.[1] According to Gurney and Mott,[2] this print-out effect supposedly occurs as follows: a photon of light ejects an electron from a chlorine ion. This electron moves about in the crystal under the influence of thermal agitation, leaving traces of neutral chlorine behind. In the course of its wandering, it is captured by some sort of trapping center (for example, a lattice defect), thus producing a net negative charge. A mobile silver ion may then migrate to this center and combine with the electron to form a silver atom. The silver atom can remain as a trap for a second electron. The second electron produces a net negative charge in this center which is neutralized by silver ion conductivity, and so on. Upon continuing this process, colloidal metallic silver is produced. The silver-halide crystal turns dark under strong light illumination over a long period. The mobility of electrons in AgCl single crystals at room temperature has been determined by Haynes and Shockley[3] by utilizing the print-out effect. The direction and velocity of photoelectrons were obtained in an electric field, and the Hall mobility of the electrons was calculated from their change in direction produced by the crossed electric and magnetic fields.

The purpose of this work was to observe directly the trace of ultrasound wave propagation in solids by utilizing the print-out effect. It is proved that there are two types of electron traps in AgCl crystals: one type, which is predominant in annealed crystals, has a very slight effect on the print-out effect when holes exist together with electrons and when an electric field is applied. The other type is associated with fresh dislocations. It serves as a good electron trap even when holes coexist with electrons and when the electric field is applied.[4]

II. EXPERIMENTAL PROCEDURES

It is impracticable to maintain a constant electric field of suitable magnitude in AgCl crystals, because the resulting steady ionic current would lead to decomposition of the salt. The average current passing through the crystals must be zero. Voltages should be applied through condensers which do not allow direct current to pass through it. However, when an electric pulse was used, even if transparent electrodes came in direct contact with the surfaces of specimens, there was no observable difference in the print-out effect. Figure 1(a) is a schematic circuit diagram of the equipment. To drive photoelectrons into AgCl specimens, a high voltage pulse was applied upward in the figure. Since the relaxation time for the electric field in AgCl crystals is on the order of 10^{-4} sec,[3] an electric pulse of 2–5-μsec duration at 29 Hz was used. The magnitude of the electric field was controlled from 0 to -10^4 V cm^{-1}. An EG and G xenon flash tube (output exceeding 0.2 J/pulse) was used to produce photoelectrons on the surface or within a crystal placed between condenser plates which consisted of nesa quartz glasses. Light sparks with a half-width of 2 μsec were set at the same repetition rate as that of the electric pulse. The speci-

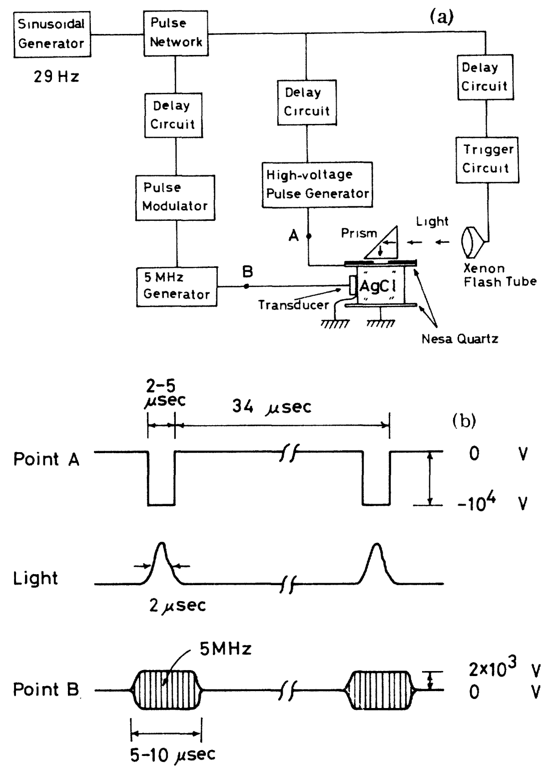

FIG. 1. (a) Schematic diagram of equipment used to generate repetitive synchronized pulses of electric field, light, and ultrasound wave. (b) Voltage forms at points A and B in the circuit and the light pulse form.

mens were illuminated through an upper nesa quartz glass with a photomask. To prevent the Herschell effect,[5] light whose wavelength was more than 650 nm was cut off with an aqueous Cu_2SO_4 filter. Toshiba Color Filters such as UV-DIC, V-Y3A, and V-03C were also used to produce light of 300–650-nm wave length.

Ultrasound waves of 5-MHz frequency were excited by 6-mm-diam X-cut quartz transducers. The duration of an ultrasound pulse at a repetition rate of 29/sec was 5–10 μsec. The magnitude of the strain due to the ultrasound waves was on the order of 10^{-8}–10^{-6}. The waves propagated in a direction perpendicular to that of the electric field and light. The pulses of the electric field, the light, and the ultrasound waves were mutually phase locked by three delay circuits with an accuracy of ±0.2 μ sec. The synchronized voltage wave forms at points A and B in the circuit and the light sparks are schematically shown in Fig. 1(b).

Single crystals of AgCl produced by the Atomergic Chemicals Co. were used. Those crystals of dimensions $1.2\times1.2\times1.2$ cm^3 had three sets of {100} faces or one set of {100} faces and two sets of {110} faces. The length of the specimen in the wave propagation direction [100] was cut to be equal to an integer multiple of one half the ultrasound wavelength. One surface (on which a transducer was bonded) and the opposite one were ground parallel to within ±0.0001 cm/cm, using dry kerosene. In this case, when waves propagating toward the right-hand side in the figure and reflected waves propagating in the opposite direction are superposed, standing waves are produced. The crystals were annealed in a vacuum at 350 °C for one week.

III. EXPERIMENTAL RESULTS

Light from the sparks fell on the top surfaces of the crystals. At this time, the electric field in the crystal was directed upward. The electrons moved downward with a velocity equal to their mobility multiplied by the electric field intensity. When pulses of the electric field and the light were applied concurrently to the annealed crystals for 26 h, in which longitudinal stationary waves were present, darkening was observed. Typical results are shown in Figs. 2 and 3. In this instance, the electric field was -5×10^3 V cm^{-1} of 2-μsec duration, the light was 300–650-nm wavelength, and the ultrasound was a 5-MHz longitudinal wave of 10-μsec duration. The length of the specimen in the direction of ultrasound wave propagation, [100], was 1.130 cm, equal to 18 times the wavelength. There were three kinds of darkening observed, as illustrated by the schematic diagram in Fig. 4. Darkening marked 1 consisted of many black planes. These planes were located perpendicular to the direction of ultrasound wave propagation in the region illuminated by the light. The distance between these planes was about 0.03 cm. Darkening marked 2 was a black plane which extended downward in an oblique direction toward a transducer from a region which was slightly apart from the edge of the

FIG. 2. Three kinds of darkening observed in an annealed crystal produced by synchronized application of pulses of electric field, light of 300–650-nm wavelength, and stationary ultrasound wave.

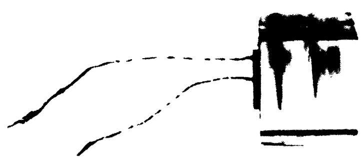

FIG. 3. Photograph of the darkening in Fig. 2 taken in a different direction.

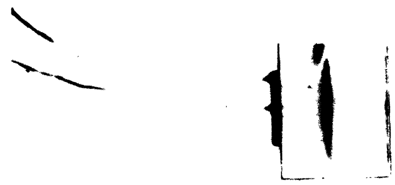

FIG. 5. Darkening in an annealed crystal produced by synchronized application of pulses of electric field, light of 300–650-nm wavelength, and a traveling ultrasound wave.

illuminated top surface. It was located in an unilluminated region in the crystals. Another darkened region, marked 3, was located in the region between a transducer and the illuminated area and was spread toward the transducer. The edge of the darkened region close to the illuminated region was very sharp. When the electric field and light pulses were applied to annealed crystals in which only a traveling wave existed, there was no type 1 darkening. However, darkening of types 2 and 3 were produced. A typical result is shown in Fig. 5. In this case, a -5×10^3 V cm^{-1} electric field of 2-μsec duration and a 5-MHz ultrasound of 10-μsec duration were utilized. The length of the specimen in the direction of ultrasound wave propagation was not an integral number of half wavelengths. The electron lifetime on or near the top surface and in the interior of a crystal was determined by using darkening of types 2 and 3, respectively. These results will appear elsewhere.[6]

IV. DISCUSSION

Darkening of type 1 occurred when an electric field and light pulses were applied to annealed crystals in which stationary ultrasound waves existed. Since the longitudinal sound velocity in the [100] direction was 3.14×10^5 cm sec^{-1},[7] a wavelength of 5-MHz frequency should equal to 0.062

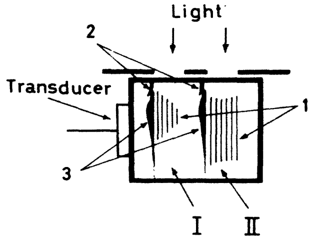

FIG. 4. Schematic diagram of the darkening in Fig. 2. Three kinds of darkening are classified as 1, 2, and 3.

cm. It is concluded that the black planes exist at a separation distance of a half wavelength. The size of the specimens was on the order of 1 cm and the distance between the planes was on the order of 10^{-2} cm. It was determined that the black planes were arranged at a distance of approximately $\frac{1}{2}n\lambda$ + 0.015 cm from the transducer. That is,

$$L \simeq (\tfrac{1}{2}n + \tfrac{1}{4})\lambda, \qquad (1)$$

where L is the distance from the black planes to the transducer, n is an integer, and λ is the wavelength. These positions correspond to the nodal plane of the wave velocity. It is determined, therefore, that the black planes are produced at the nodal planes of the ultrasound wave velocity.

According to the theory by Gurney and Mott,[2] electrons, silver ions, and electron traps such as lattice defects play an important role in the process of the print-out effect. Electrons might be considered to gather in the nodal planes of stationary ultrasound waves because of the field due to the deformation potential. However, since the magnitude of the ultrasound-induced strain is on the order of 10^{-8}–10^{-6} and the deformation potential for AgCl crystals is on the order of 1 eV,[8,9] the change in energy due to the wave is on the order of 10^{-8}–10^{-6} eV. This value is much smaller than that of thermal energy at room temperature. Therefore, it is reasonable to conclude that the movement of electrons will not be affected by a small strain induced by the ultrasound waves and the darkening is not produced by electrons which are controlled by these standing waves.

Silver ions may be controlled by ultrasound waves; some of the interstitial silver ions in the antinodal planes are moved into nodal planes and grow into colloidal silver through a succession of recombination with electrons. However, the strain energy of the ultrasound wave in this experiment was on the order of 10^{-5}–10^{-1} erg cm^{-3}. Since the number density of interstitial silver ions at room temperature is on the order of 10^{16} cm^{-3},[10] the effect of ultrasonic strain energy on a silver ion is on the order of $10^{-21}-10^{-17}$ erg, or $10^{-10}-10^{-6}$ eV. However, the activation energy for silver-ion conduction is about 1 eV.[11] Thus, a change in energy of the silver ions due to ultrasound waves is negligible compared with the activation energy. It is also thought that the darkening is not affected by silver ions controlled by the standing wave.

The type 1 darkening can be explained in terms of the movement of dislocations. Slip occurs at room temperature in AgCl on a $\{110\}$ plane along a $\langle 110\rangle$ Burgers vector, as in most crystals of the rocksalt structure. Uniaxial load applied parallel to a $\langle 100\rangle$ direction produces slip on four of six possible $\{110\}$ faces. Maximum shear stress $\tau(\langle 110\rangle)$ due to the $\langle 100\rangle$ load is exactly parallel to the four glide directions. When longitudinal standing waves with amplitude $\sigma(\langle 100\rangle)$ are induced in a crystal with the displacement x parallel to $\langle 100\rangle$, the resulting shear stresses $\tau(\langle 110\rangle)$ are given by

$$\tau(\langle 110\rangle) = \sigma(\langle 100\rangle)\cos\theta\cos\phi\,\sin(2\pi x/\lambda)\sin\omega t = \tfrac{1}{2}\sigma(\langle 100\rangle)\sin(2\pi x/\lambda)\sin\omega t\,, \quad (2)$$

where θ is the angle between the normal to the glide plane and the axis of the load, ϕ is the angle between the glide direction and the axis of the load, λ is the wavelength, and ω is the frequency. Dislocations with a density of ~10^5 cm^{-2} in these crystals remained after they were well annealed. Some of these dislocations are moved to nodal planes by the shear stress of the stationary wave. The displaced dislocations are fresh, and they act as good electron traps. Electrons are captured by these fresh dislocations which are arranged in the nodal planes of the standing ultrasound wave, producing net negative centers. Mobile silver ions migrate to the centers and combine, forming silver atoms, and so on. Then the dislocations are locked at the dis-

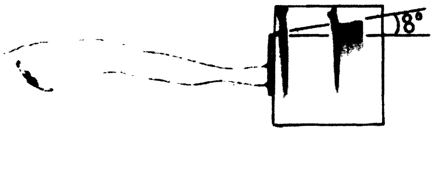

FIG. 6. Darkening in an annealed crystal produced by synchronized application of pulses of an electric field, light of 300–650-nm wavelength, and ultrasound waves.

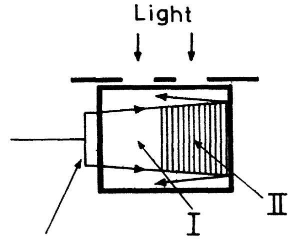

FIG. 7. Expected schematic diagram of ultrasound wave propagation in Fig. 6 while the electrons are free.

placed positions by colloidal silver atoms. Since the dislocation velocity in ductile crystals such as Cu and AgCl is on the order of 10^3 cm sec^{-1} for the existing strain range,[12] it is estimated that dislocations are moved by a ~10^{-3} cm during a ~5-μsec ultrasound wave pulse. This value of dislocation displacement may give a reasonable explanation for interpreting the distance between the black planes. It was also noticed that the optical density of the darkened regions was roughly equal to that of slightly deformed crystals.[4] Therefore, it is concluded that those dislocations which are moved by a stationary ultrasound wave play an important role in producing the darkening effect.

Because the strain was on the order of $10^{-8}-10^{-6}$, it is believed that the stress does not reach a critical value beyond which dislocation sources produce new dislocation loops.[13] It was confirmed by observation of etch pits that the dislocation density in these crystals did not change by applying ultrasound waves.[14]

It took about 4 μsec for the wave to travel from surface to surface in the crystals. The timing when the wave is applied is as important as the parallelism and the length of specimens. A typical result is shown in Fig. 6 when the ultrasound wave pulse of 10-μsec duration was applied 1 μsec subsequent to application of the electric field and light pulses. In this case, the electric field was -5×10^3 V cm^{-1} of 2-μsec duration. The length of the specimen in the direction of ultrasound wave propagation [100] was 1.256 cm, equal to 20 times the wavelength. The expected propagation of the wave in Fig. 6 during the time that electrons are free is presented schematically in Fig. 7. The electron lifetime in the interior of crystals was determined to be about 5 μsec by using type 3 darkening.[6] Waves excited on the left-hand surface are reflected by the right-hand surface and arrive at the middle of the specimen while the electrons are free. Vertical lines show the nodal planes of the stationary wave. The stationary wave exists in area II, but only a traveling wave exists in area I.

The shape of the darkening in Fig. 6 is very similar to the upper part of the expected trace of the stationary wave in area II of Fig. 7. Thus it is concluded that the darkening in Fig. 6 represents a part of the trace of the stationary wave in AgCl crystals. Furthermore, as can be seen in Fig. 7, the trace of the stationary wave corresponds to that of the traveling wave which propagates toward the right-hand side. It is also concluded that the darkening in Fig. 6 is the first direct observation of a part of the trace of the ultrasound wave propagation in solids. On the other hand, the darkening is hardly observed in the lower part of the specimen in Fig. 6. This is due to the fact that electrons were not displaced in the lower part of the specimen by the electric field.

A velocity potential Φ from the transducer which is produced by a circular transducer bonded to a solid material and propagates in it, can be represented by the formula[15]

$$\Phi = (Vd^2/4\gamma)\left|[J_1(Z)/Z]\right|, \quad Z = (\pi d/\lambda)\sin\theta, \qquad (3)$$

where V is the sound velocity, d is the diameter of a transducer, γ is the coordinate, $J_1(Z)$ is the Bessel function, λ is the wavelength, and θ is the angle between the propagating direction of an ultrasound wave and the normal to a transducer. A directivity function D, which represents the wave-propagating direction, is written as

$$D = \left|[2J_1(Z)/Z]\right|. \qquad (4)$$

An approximate calculation of D can be effected in the present case, assuming the following values: $d = 6\times10^{-1}$ cm and $\lambda = 6\times10^{-2}$ cm. Then, D becomes zero when $\theta = 7°$. On the contrary, as is seen in Fig. 6, the ultrasound waves excited in the [100] direction propagate radially within an angle of about 8° from the normal to the transducer. This magnitude is very close to the value calculated from Eq. (4). It is considered that a longitudinal ultrasound wave propagates in the [100] direction of AgCl crystals as it would propagate in an isotropic medium.

The upper edge of the darkening in Fig. 2 is not as clearly defined as that in Fig. 6. In Fig. 2, the ultrasound wave pulse was applied by about 3 μsec prior to application of the electric field and light pulses. The wave first reflects on the right-hand surface, and then on the left-hand surface on which a transducer is bonded. It arrives at the middle of the specimen while electrons are free. The waves are superposed three times. There are two kinds of stationary waves—one consists of a wave propagating toward the right-hand side and the first reflected wave propagating in the opposite direction. The other stationary wave consists of a wave reflected on the right-hand surface and a wave reflected on the left-hand surface. That is, these two stationary waves are superposed. The amplitude and trace of the superposed stationary wave are considered to vary as a complicated function of the position and the time. It is considered that this superposition of the standing waves is the origin of the diffuse darkening of the upper edge of the crystal shown in Fig. 2.

V. SUMMARY

The effect of ultrasound waves on the print-out effect in AgCl crystals was studied at room temperature. When a longitudinal standing ultrasound wave was generated in a crystal during application of electric field and light pulses, black planes caused by the print-out effect were produced. These planes were located in the nodes of the stationary ultrasound waves and were perpendicular to the direction of the wave propagation. The distance between the darkened planes was roughly equal to half the wavelength of the ultrasound wave. It is concluded that the darkening is a result of the print-out effect due to fresh dislocations caused by the stationary longitudinal waves. The trace of the ultrasound wave propagation is clearly made evident by the darkening and represents the first direct observation of the wave-propagation trace in solids. However, a traveling wave did not have an effect on the print-out effect.

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FIG. 3. Photograph of the darkening in Fig. 2 taken in a different direction.

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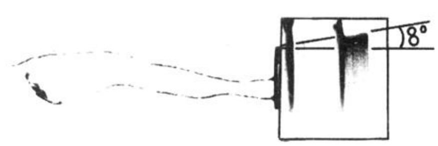

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