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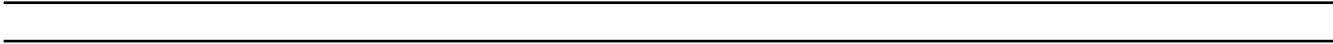
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Noble metal impurities have been observed to segregate toward the surface of p-type CdTe and heavily p-type (Hg,Cd)Te samples during room temperature aging in ambient room light. This behavior has not been observed in n-type CdTe or lightly p-type (Hg,Cd)Te. The photon-induced segregation is believed to involve the redistribution of positively charged impurity interstitials in a field generated by absorbed photons with energies greater than the band gap. A qualitative electromigration model based on the Dember effect and simple ionic conduction, has been used to explain the experimental results.

I. INTRODUCTION

Both lasers and heat lamps have been used to distribute dopant impurities in semiconductors. In these cases, the dopant diffuses down a concentration gradient as the result of heating. In contrast to this behavior, we have observed an unusual case of nonclassical diffusion in which Ag impurities have been found to migrate up a concentration gradient and segregate near the surface of CdTe during exposure to ambient room light.[1] This behavior has been more extensively investigated in both CdTe and (Hg,Cd)Te and is qualitatively modeled in the present paper.

II. EXPERIMENTAL

Samples of CdTe and (Hg,Cd)Te were prepared by electroless plating of radioactive ^{110m}Ag from dilute nitric acid solutions, and annealing for longer than 15 min to partially distribute the Ag isotope. Tracer profiles were measured by incrementally etching samples with a freshly prepared 0.5% Br-methanol solution, and counting the amount of tracer present in each increment with a NaI well detector. The measured background for the detector was about 1 cps. Periodically, the sample was weighed to establish an approximate etching rate, which was found to be roughly 1.5 μm/min for CdTe. Etch increments were usually obtained by etching for 2 min, with approximately 1–2 min elapsing between consecutive etches, unless the samples were intentionally aged or weighed.

III. RESULTS

Segregation of Ag to the CdTe surface region was intially discovered after weighing the sample to establish etch removal rates. The profile in Fig. 1 shows the Ag intensity after consecutive etch steps and after weighing. Anomalous increases in the Ag intensity by a rough factor of 3–8 times were observed after either weighing or intentionally aging for 30–36 min. Additional etches for 2 min showed the Ag intensity returned to the same level established by etching prior to aging. When the sample was aged for 30 min at 77 K, the accumulation of Ag at the surface was suppressed, as indicated by the figure. Following an additional 36 min aging at room temperature, a 10 s etch was performed which

removed more than half of the segregated Ag. Another immediate 2 min etch removed the remaining portion of the segregated impurity. This result implies the segregated Ag extends over a short depth beneath the surface, rather than being exclusively concentrated at the surface.

To examine the dependence of the segregation on surface chemical reactions, such as oxide formation, samples were aged under carbon tetrachloride in order to eliminate the exposure to air during aging. Ag pile-up was still found to occur even though the oxidizing ambient was removed. A second experiment was performed using radioactive ^{198}Au, since Au does not oxidize in air. The profile for Au in CdTe before and after aging is shown in Fig. 2. Segregation of Au was observed initially after aging for 28 min, but was not observed with additional aging for 15.5 h and 6 h. Unlike the Ag impurities which retained their ability to segregate for weeks after the samples have been aged at room temperature, the ability of Au to segregate appears to decay after being held at room temperature for much shorter periods of time, as indicated by the figure. Since the observed mobility of both Ag and Au impurities occurs at temperatures too low for vacancy diffusion, the impurities are assumed to mi-
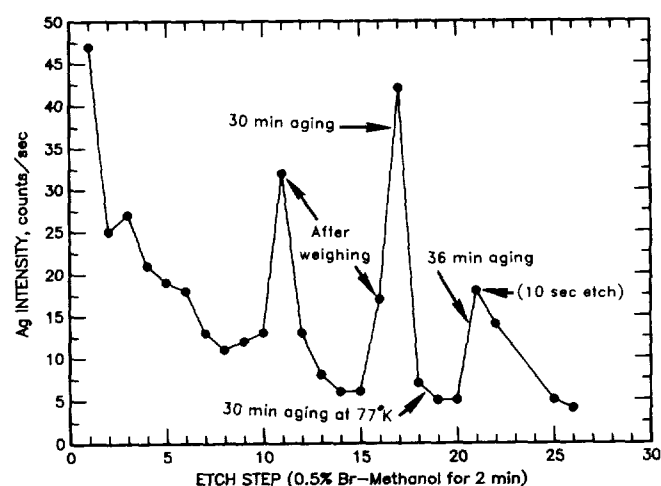

FIG. 1. Ag tracer profile of doped p-type CdTe showing surface segregation of Ag after room temperature aging. ^{110m}Ag-doped CdTe annealed at 270 °C for 1 h.
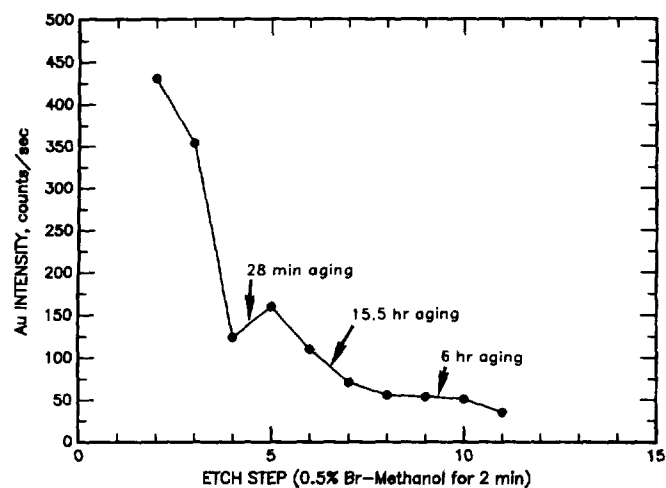
FIG. 2. Au tracer profile in CdTe showing surface segregation after 28 min aging. [198]Au-doped CdTe annealed 15 min in vacuum at 270 °C.

grate as interstitials. Different interstitial densities for Ag and Au may account for the dissimilar magnitudes of segregation, and suppression of segregation may result from a reduction of the density of impurity interstitials.

The dependence of the Ag out-diffusion on ambient light has been previously communicated.[1] Ag-treated CdTe samples were aged alternately at room temperature in ambient room light, or in darkness while wrapped in aluminum foil. The experimental aging profile in Fig. 3 shows that Ag segregation is suppressed during storage in darkness. This result suggests either photoinjected carriers, or a photoinduced potential may be responsible for the redistribution of Ag interstitials, and material properties may therefore influence impurity segregation.

In order to investigate the influence of material type, a piece of the as-grown p-type CdTe material used for the previous measurements was preannealed at 800 °C for 1 week in saturated Cd vapor prior to being treated with radioactive Ag. This anneal has previously produced n-type CdTe, as determined by Hall measurements.[2] The sample was then
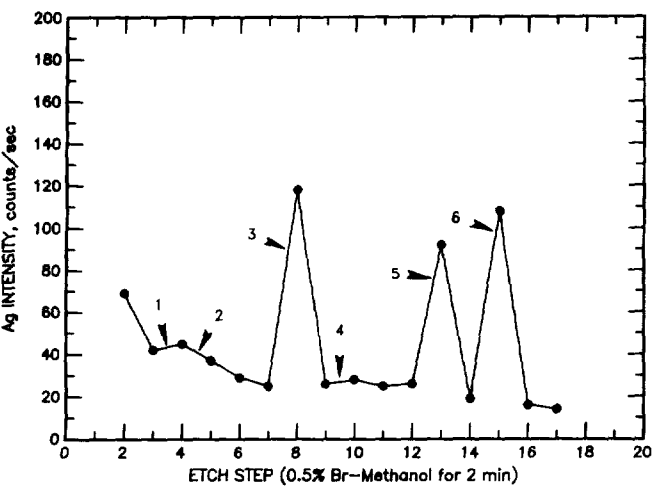

FIG. 3. Ag tracer profile in CdTe showing segregation as a function of exposure to light. (1) 10 min aging in light, (2) 48 min aging in darkness, (3) 62 min aging in light, (4) 64 min aging in darkness, (5) 71 min aging in light, and (6) 16 h aging under variable illumination (see text).
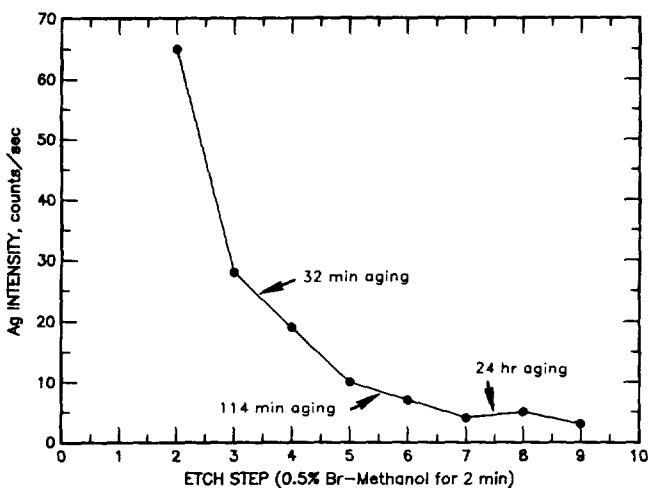
FIG. 4. Ag tracer profile for n-type CdTe showing absence of segregation. CdTe preannealed at 800 °C in Cd vapor for 1 week; treated with [110m]Ag and annealed at 270 °C for 16 h.

treated with Ag and annealed at 270 °C for 16 h in an ampoule with excess Cd. An aging profile for this sample, shown in Fig. 4, indicates a suppression of the Ag out-diffusion by the preannealing treatment, since no macroscopic increase in Ag intensity is observed after aging. No significant Ag segregation was observed after aging for either 32 or 114 min, but a slight amount of segregation may have occurred after aging for 24 h, as indicated by the figure.

To complement the measured Ag aging profiles in CdTe, similar measurements were performed in (Hg,Cd)Te containing about 20% Cd. Both as-recrystallized p-type and postannealed n-type materials were treated with Ag and profiled, however, no segregation was evident in either case. Since this narrow band gap material exhibits a Hall coefficient which is negative (i.e., like n-type) at room temperature even when the material is p-type at 77 K, segregation of Ag may be small or absent, as in the case of the CdTe in Fig. 4. In an attempt to make the (Hg,Cd)Te sufficiently p-type to observe this effect, a piece of the material was saturated with nonradioactive Au at 270 °C in an evacuated ampoule prior to being treated with radioactive Ag. The aging profile for Ag measured in this extrinsically p-type sample (with an acceptor density of about 1×10^{18} cm^{-3}) is shown in Fig. 5. The incremental Ag concentration was observed to increase after both 30 min aging and 73 min aging, but had fully relaxed after several days. The relatively small amount of segregation of the Ag may be offset by much more segregation of the nonradioactive Au that was present in this sample.

IV. DISCUSSION

The absorption of photons with energies greater than the band gap generates excess electrons and holes that can redistribute within the semiconductor material. If the mobilities of both types of carriers are equal, then interband recombination will occur without charge separation. Alternatively, if these mobilities are different and absorption is close to the surface, then charge separation can occur which produces a potential gradient parallel to the direction of the absorbed light. This phenomenon is known as the Dember effect.[3,4] In cases, such as CdTe and (Hg,Cd)Te, where the electron mo-
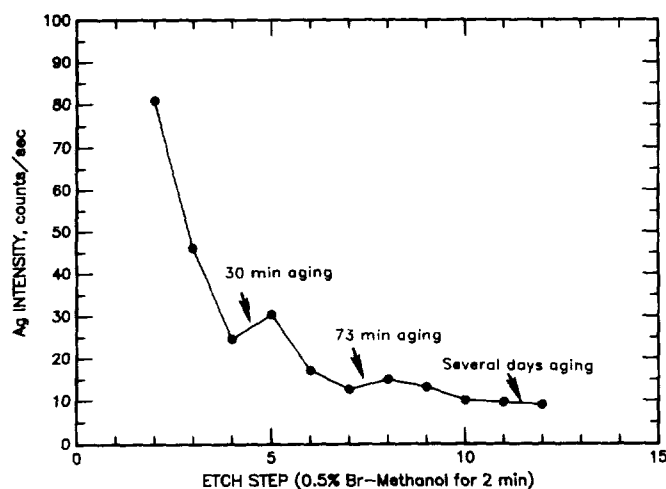
FIG. 5. Ag tracer profile in heavily p-type (Au saturated) (Hg,Cd)Te containing 20% Cd. Au-saturated HgCdTe treated with ^{110m}Ag annealed at 270 °C for 15 min in vacuum.

bility is larger than the hole mobility, electrons will be injected into the bulk while excess holes will be left near the surface, i.e., the surface tends to become more positive relative to the bulk. Some of the photoinjected electrons will diffuse away from the surface into the bulk until annihilation, presumably by recombination processes. Under continuous illumination, a Dember voltage will persist, and charged mobile impurities may redistribute in the presence of this photoinduced field.

For the purpose of establishing a qualitative model, it is assumed that the mobile Ag impurities are interstitials with a positive effective charge. This is a reasonable assumption, since Ag has been found to migrate toward the negative electrode when a current is passed through (Hg,Cd)Te.[5] Moreover, noble metals have exhibited electromigration behavior in other semiconductor and metal systems.[6] (Shewmon[7] has treated electrolysis of interstitial impurities in solids, and has discussed the interpretation of the effective charge.) In this case, the redistribution of the positively charged Ag interstitials can then be simply treated as ionic conduction, with Ag ions migrating toward the surface in opposition to the photoinjected electrons which are diffusing into the bulk. Ag should collect where the net electron density is a maximum. Although the position of the peak Ag density relative to the surface has not been accurately determined, the 10 s etching result in Fig. 1 suggests it may lie within roughly 0.25–0.30 μm from the surface, since more than half the segregated Ag was removed by etching to this depth. Lower Ag densities are expected at the surface, since it should tend to have a higher density of holes and be more positively charged.

The ionic conduction or electromigration model should also be examined with regard to the apparent type dependence of photon-induced segregation in both CdTe and (Hg,Cd)Te. Experimental evidence suggests segregation is only observed in materials which are strongly p-type at room temperature. If the electron concentration gradient is the chief factor for inducing positive impurity ions to migrate toward the surface, then photon absorption should produce a large electron concentration gradient in materials with a small donor concentration (i.e., p-type materials). Large

electron gradients could also be produced in n-type materials as well, providing there is sufficient incident photon density. Alternatively, if there is insufficient illumination, the high majority carrier electron concentration will result in a much smaller electron gradient, and the photon-induced segregation may be too small to be observed in the n-type material. Illumination in ambient room light may fall into this latter case, but more experimental work is necessary to test this hypothesis.

Lastly, the (Hg,Cd)Te results need to be addressed in the context of the extremely small band gap, which is nominally 0.1 eV. Ag segregation has not been observed in p-type material which is lightly doped, but has been observed in Au doped material (in Fig. 5) which is heavily p-type. If thermally generated carriers predominate, so that the material is nearly intrinsic (i.e., the number of electrons equals the number of holes) the material will appear to be n-type at 300 K as evidenced by a negative Hall coefficient, even though the material may be p-type at 77 K. In this case, the high mobility electrons dominate conduction at room temperature, in spite of being the minority carriers. Under these circumstances, the thermally generated electron population may be sufficiently high so as to reduce the photon-induced electron gradient and suppress the out-diffusion of Ag. This scenario should prevail in lightly doped p-type (Hg,Cd)Te. By heavily doping the material with Au so that it appears to be strongly p-type at room temperature (as determined by Hall measurements) the equilibrium electron concentration may be small enough so as to permit incident photons to produce a large electron gradient. Experimentally, Ag segregation has been observed under these heavily p-type conditions. Therefore, photon-induced electromigration appears to require a sufficiently low minority electron concentration to be observed.

The ionic conduction model for the electromigration of positively charged Ag interstitials has been qualitatively rationalized to explain both a graded subsurface Ag distribution and the observed type dependence in CdTe, as well as the apparent effect of the band gap in (Hg,Cd)Te. The physical description of the ionic conduction model for the segregation behavior of Ag impurities needs additional scrutiny, and eventually quantitative modeling. Nonetheless, the experimental results in CdTe and (Hg,Cd)Te are consistent with a photon-induced electromigration of charged Ag interstitials. Consequently, a portion of the Ag must exist as interstitials for this effect to be observed at room temperature. Finally, this phenomenon may also induce segregation of other fast-diffusing interstitial impurities.

V. CONCLUSIONS

Photon-induced segregation of radioactive Ag has been observed in both p-type CdTe and strongly doped p-type (Hg,Cd)Te, while samples are held at room temperature in ambient room light. Segregation has not been observed in either n-type CdTe samples, or weak p-type (Hg,Cd)Te samples. This effect appears to involve the redistribution of positively charged interstitial Ag impurities during the redistribution of photoinjected electrons, and is not associated with surface chemical reactions. A qualitative electromigra-

tion model based on the Dember effect and simple ionic conduction, can be used to explain the experimental observations.

ACKNOWLEDGMENTS

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