EXPLOSIVE CRYSTALLIZATION OF RF-SPUTTERED
AMORPHOUS CdTe FILMS

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Explosive crystallization of about 2-μm thick amorphous CdTe
films prepared by rf-sputtering in an Ar-N_2 ambient has been
observed. The transformation can be initiated with or with-
out external thermal or mechanical impulses depending on the
oxygen content of the films. The crystallization is accom-
panied by a light flash. X-ray diffraction, Auger analysis,
and resistivity measurements were made on these films to
arrive at a qualitative model to explain the observations.

Key words: explosive crystallization, amorphous semiconduc-
tors, rf-sputtered films.

Introduction

"Explosive" amorphous-to-crystalline transformations in
sputter-deposited amorphous Ge films were first reported by
Messier et al. [1-6] Their study of the phenomenon occurring
at room temperature showed that the transformation is highly
exothermic and that the crystallization of the entire sample
occurs by a series of "microexplosions," in which both an
initiation and a propagation mechanism were identified. The
crystallization could be initiated by any localized energy
impulse such as (i) laser pulsing or e-beam; (ii) touching

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with a heated glass tip or microtorch (thermal); or (iii)
pricking with a sharp point (mechanical). The propagation
velocity is reported to be on the order of 120 cm/sec and in
this process an estimated bulk temperature of 500°C is
reached. [4] Explosive crystallization could be quenched by
lowering the sample temperature to 78 K. Their results were
later confirmed by Kikuchi et al. [7,8]

    Wickersham et al. [9] reported a similar observation on
what they termed "impulse-stimulated crystallization" in
sputter-deposited amorphous (In,Ga)Sb films. Their results
indicate that a minimum temperature T* is needed for micro-
explosions to propagate and that T* depends on the film com-
position as well as the thermal annealing history of the film.
Further, T* was observed to be above room temperature with T*
increasing for higher pre-annealing temperatures and longer
pre-annealing times. The propagation velocity of the trans-
formation was on the order of 200 cm/sec. The explosive
crystallization in these alloys was always found to be asso-
ciated with large changes in sample resistivity and reflec-
tivity.

    Based upon the work in the above studies, Fan et al. [10]
showed that by more precisely controlling the propagation of
laser-initiated explosive crystallization, through regulation
of both film temperature and laser power density, very large
crystallite-sized Ge films could be prepared. Thus the
potential exists for obtaining large crystallite-size, or
even single crystal, films of Ge and other semiconductors on
inexpensive, large area substrates.

    In this paper we report the preparation of a particular
set of noncrystalline (or amorphous) CdTe films prepared in
an Ar/N_2 sputtering gas atmosphere, hereafter designated as
a-CdTe:N, which also show this explosive crystallization
phenomenon. The crystallization occurred spontaneously
during initial exposure to ambient conditions in our earlier
experiments but subsequently could be controlled and stimu-
lated externally by both mechanical as well as thermal means.

                              Experimental

    Films were sputtered from a 5" dia hot pressed target
(99.99% purity) using an MRC rf-sputtering system with a
residual background pressure $\sim 10^{-7}$ torr. A mixture of

purified Ar at 20×10^{-3} torr pressure and Linde UHP grade N_2
(purity quoted by manufacturer was 99.999% with oxygen
< 1 ppm and moisture < 3 ppm) at a flow rate of 20 std
cc/min ($\sim$ 4 to 5 x 10^{-3} torr) was employed. The substrate-
to-target distance was fixed at 40 mm, and the rf-power
density was maintained at 0.4 watts/cm^2 in obtaining the
2-μm thick films. Ultrasonically cleaned glass slides
(Fisher 12-549) and fused silica cover slips were used as
substrates. No substrate heating or cooling was employed.
However, in the steady state, substrate temperatures $T_s \sim 80-$
100°C were recorded, as measured by a thermally aged and
calibrated noncrystalline Ge thermistor-type film, agreeing
with the observation by Gilbert et al. [15] After deposi-
tion the films were usually kept under vacuum for several
hours allowing T_s to come to room temperature before removal
from the system. However, on breaking the vacuum and on
removal from the vacuum chamber the films appeared grayish
and the substrate platform was unusually warm. Even a
cursory inspection of these CdTe:N films revealed features
characteristic of explosively crystallized (EC) a-Ge films.
The spontaneous crystallization of these a-CdTe:N films had
evidently occurred during exposure to the atmosphere, and
further it was found that they were highly reproducible and
independent of the gas leaked into the vacuum chamber for
their removal. This behavior, however, was not observed for
a-CdTe films prepared by sputtering in a pure Ar atmosphere.
This transformation, while the sample is inside the chamber
(in-situ explosive crystallization--IEC), should be distin-
guished from the a-Ge and a-(In,Ga)Sb cases in which crys-
tallization was achieved only by external triggering (ex-
situ explosive crystallization--EEC). Further, the as-
sputtered noncrystalline films changed from a translucent,
reddish-yellow to gray upon transformation.

Results and Discussion

It was found that even trace levels (ppm range) of
oxygen impurities in the gas stabilized the films so that
they could be removed from the chamber without spontaneous
crystallization. Once such a film is taken out of the
vacuum system, EEC could be initiated by any means similar
to that for the case of explosive Ge. By carefully con-
trolling the oxygen content in the sputtering chamber during
sputtering, even more stable films that would not transform
at room temperature could be prepared. However, on raising

the temperature of such samples to 80°C and simultaneously
applying a mechanical impulse, the films could be made to
explosively crystallize. The critical temperature T* thus
seems to depend on the partial pressure of oxygen during
preparation. Increasing oxygen content well beyond trace
level completely stabilized the film to a point that no EC
could be triggered. Further, even the partially stable
films that would otherwise have exploded at room temperature
on mere mechanical contact, tended to stabilize on exposure
to air over a period of time. The longer they were exposed
the more stable they became indicating a metastability
decrease induced by postdeposition oxidation. When these
partially stable films were immersed in water or liquid
nitrogen no EC could be generated.

In addition to a change in color, both IEC and EEC were
accompanied by a flash of light (estimated in the milli-
second duration range) with sufficient intensity, and
thereby enabling us to photograph the inside of our sputter-
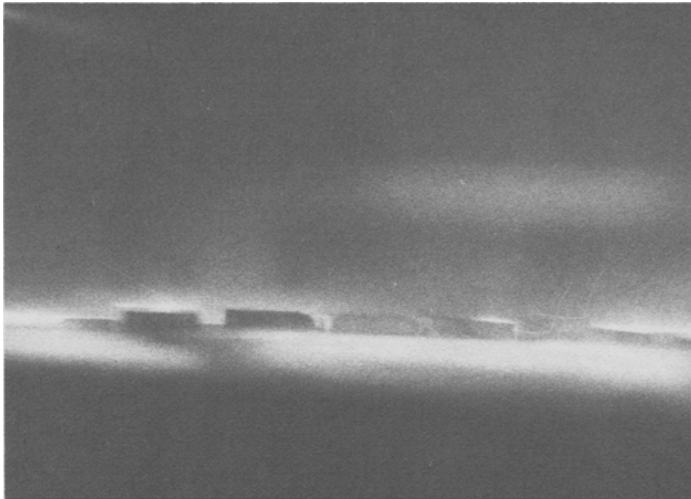ing chamber without any additional illumination. Figure 1

Fig. 1. A photograph showing the substrates
placed on the platform inside vacuum chamber.
This picture was taken with the camera wide
open and using only the light flash from ex-
plosive crystallization and no other light
source.

shows such a picture taken with a Pentax (f/1.4 lens) camera
using high speed recording film, Kodak RE-135 (1600 ASA).
The picture shows four fused silica substrates (9 mm x 9 mm)
arranged on a platform. Our preliminary attempts at spec-
trographic characterization of the flash were not successful.
A more systematic attempt is planned for the future. Fur-
ther, for EEC a black "smoke" followed the flash.

In order to study the effect of the substrate, films
were deposited on various substrates (e.g., fused silica,
Mo, glass, stainless steel, Au, Cu, and Al) covering a wide
range of thermal expansion and thermal conductivity. All
films regardless of substrate, exhibited both in-situ as
well as ex-situ crystallization depending on the oxygen
content. Finally, the electrical resistivity ρ was measured
with sputtered Ni contacts on the films. While resistivity
for a-CdTe was $\sim 10^6$ Ω-cm, EC films were ~ 40 Ω-cm, lower by
more than 5 orders of magnitude. Wickersham et al. [9]
reported a similar observation with their (In,Ga)Sb films,
although the resistivity dropped only by 3 orders of magni-
tude in their experiments.

X-ray diffraction patterns (Fig. 2a) of non-transformed
films revealed its amorphous nature, while explosively crys-
tallized films showed sharp diffraction peaks corresponding
to both sphalerite and wurtzite (cubic and hexagonal, re-
spectively) phases of CdTe. Figure 3 is an SEM micrograph
of an EEC CdTe:N film, the surface of which appears general-
ly covered with crystallites on the order of 0.1 μm and
agglomerates on the order of 1 μm. Near the sites of EC
initiation, however, agglomerates nearly ten times larger
are found. Another sample which appeared less grayish to
the eye also had 0.5 μm agglomerates but fewer in number.
When the agglomerates are on the order of the wavelength of
light and closely spaced, the surface has a graded refrac-
tive index leading to high light absorption. Such light
scattering results in the grayish appearance.

Auger Electron Spectrometry (AES) was used to determine
the chemical compositions of several amorphous (i.e., unex-
ploded), IEC, and ECC films, and typical results are given in
Table 1. In addition, Auger scans were carried out on the
materials which were ejected during an ex-situ explosion and
collected on a nearby copper substrate. The Auger spectra
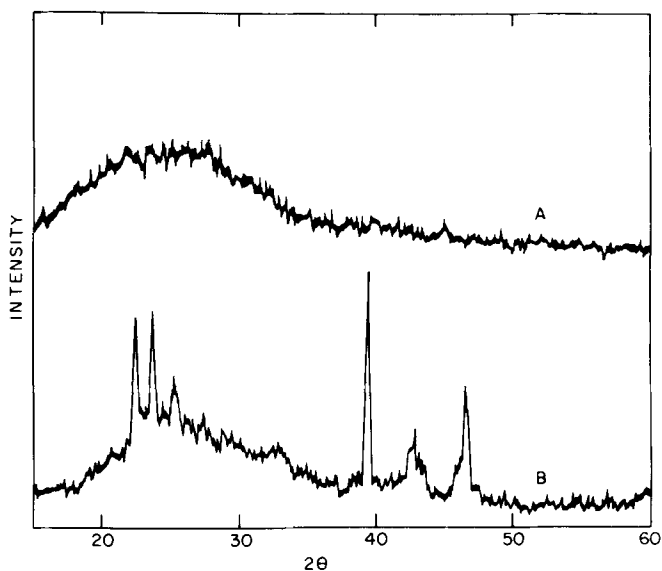in the derivative mode were recorded using a 1.5 keV, 20 μA

Fig. 2. X-ray diffraction pattern of (a) as-deposited CdTe film on fused silica substrate showing amorphousnature, and (b) explosively crystallized film revealing various diffraction peaks.

Table I.   Nature and Composition of Representative Films

Sample #	Nature	AES Atomic Concentration			N₂ Purity
		Cd	Te	O	
KO20	IEC (highly unstable)	41	58	1	*
KO19	Exploded film collected	34	64	2	**
	on to Cu foil	37	61	2	**
KO16	EEC (partially stable)	41	54	5	**
KO17	Stable amorphous film (crystallized only above 80°C)	49	37	14	**

*   Ultra-high purity (99.999% with < 1 ppm O_2)
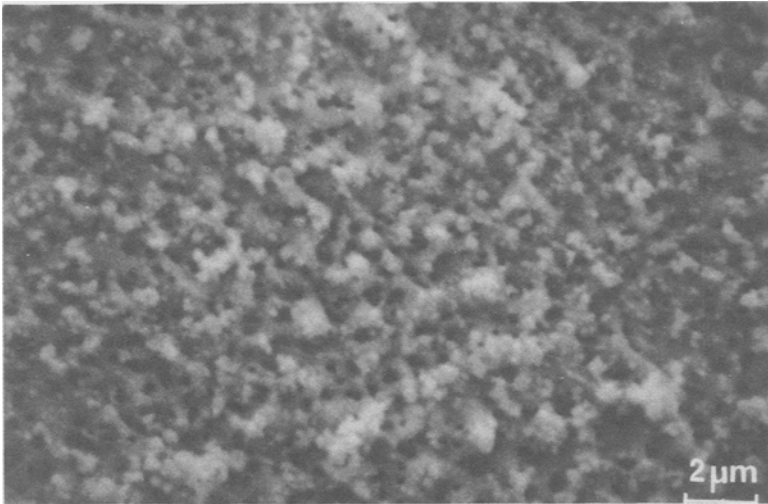**   High purity (99.99% with > 3 ppm O_2)

Fig. 3. SEM photograph of top surface of an
explosively crystallized film.

primary electron beam. Surface composition was evaluated
from the Auger data using Eq. (8) of Ref. 16

$$C_x = \left(\frac{I_x/k_x}{\sum\limits_i I_i/k_i} \right) \tag{1}$$

where I_x is the Auger peak-to-peak signal, C_x is the concen-
tration of element X, k_x is the sensitivity of X relative to
an arbitrary standard, and the summation is over all the ele-
ments present. In this study, the Cd-376 eV, Te-483 eV and
0-512 eV Auger peaks were used. Auger sensitivities for 0
and Te relative to Cd were evaluated from MgO, Te and Cd
standards as in Ref. 16. The applicability of Eq. (1) was
demonstrated recently by Tongson et al. [17] in determining
the composition of densified WC-Co composite material.

    A careful anlaysis of Auger data gave no conclusive
indication of the presence of nitrogen in the films. A draw-
back of AES for the CdTe:N system is that the Cd-382 eV peak
interferes with the KLL transition of N at 381 eV. However,
the presence of N may be inferred by comparing the Cd 382/
Cd 376 ratio obtained from the films with the corresponding

ratio from elemental Cd. In our case these two ratios agreed
to within experimental error.

    Table I shows typical Cd, Te and O concentrations as a
function of the nature (i.e., amorphous, IEC, ECC) of the
films and the ambient conditions during deposition. The
precision of the normalized concentrations is better than 1%.
From Table I it appears that the IEC films contained the
smallest amount of oxygen and stable amorphous films contain
a larger fraction of oxygen, possibly incorporated as CdO.
During explosion CdO may dissociate, resulting in a lower
oxygen content in the collected deposit.

    The above observations can be explained by an extension
of the model proposed for a-Ge. [2,4,5] This crystallization
phenomenon consists of two distinct mechanisms, an initiation
and a propagation mechanism. The initiation is controlled
primarily by the metastable state of the noncrystalline films,
while the propagation is controlled not only by this struc-
tural metastability (and the net energy gain during transfor-
mation on an atomic scale), but also by the efficiency of
transfer of this energy from atom-to-atom on times $\sim 10^{-10}$ sec.
The observation that a continuous range in a-CdTe:N film
metastability is found (as manifested in its crystallization
behavior) and understood in terms of oxygen stabilization
then gives us a clue as to the initiation mechanism.

    The as-deposited, amorphous CdTe:N films are in a highly
metastable state requiring a relatively small activation
energy for transformation to the crystalline state as compared
to the net energy gained during the crystallization. It is
not uncommon that thin films undergo a change in stress state
upon exposure to air. For instance, Paesler [18] has observed
a reduction in tensile stress on exposing freshly evaporated
a-Ge films to moist air and attributes this to water adsorp-
tion or oxidation. Recently, Tsai and Fritsche [19] have
shown that a-Si films adsorb 6.5 mol% water within 1 min
after air exposure and 12 mol% after 16 hrs and attribute
the behavior to the well-documented void network structure
in such materials.

    The proposed explanation then follows. Upon initial air
or controlled atmosphere exposure, gases or water vapor are
physisorbed on all surfaces (including internal voids origi-
nating at the film surface) causing a change in the stress
state particularly over a thin top layer of the film. When

the film has a low oxygen content, a sufficiently high
metastable state exists such that this stress change initiates
the IEC behavior. As various films are prepared with higher,
controlled oxygen contents this metastability decreases to
the point that this atmosphere-exposure induced stress
change is not sufficient to initiate EC. This marks the
change between IEC and ECC behavior. If any small, localized
mechanical stress is immediately applied, EEC occurs. How-
ever, if the application of this mechanical stress is delayed
after air-exposure, a larger amount of external force is re-
quired to initiate EC, the necessary force increasing with
exposure time. Thus postdeposition oxidation appears to be
continually stabilizing the initially highly metastable
films. In fact, after approximately a one-day exposure to
air the EC could no longer by initiated.

    In this connection, the recent study by Kennealy et al.
[22] on chemiexcitation between metastable atomic nitrogen
and molecular oxygen which is also a largely exothermic
reaction, is relevant. They find that the observed IR
radiation corresponds to an N-O vibrational spectra created
solely by the chemcial reaction, unaffected by any relaxation
process. It is interesting to note that they compute the
energy released to be anywhere from 1 to 4 eV depending on
the reaction path. Such a mechanism could account for both
the explosive crystallization of CdTe:N films and the accom-
panying light flash.

    In summary, we have prepared CdTe:N films that
explosively crystallize, the explosive nature of which is
dependent on the preparation history, in particular the
oxygen content in the ambient as well as the post-oxidation
treatment. While the phenomenon is similar to that observed
in a-Ge films, the striking feature is that it takes place
for much thinner films-EC in Ge needed $\sim$20-μm whereas EC in
CdTe:N is possible in a 2-μm thick film. Further, the
extent of crystallization is also large compared with a-Ge.
A more detailed study relating this phenomenon to the film
microstructure and nanostructure will be reported elsewhere.

Acknowledgment

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