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INFERIOR ELECTRONIC PROPERTIES OF RF-SPUTTERED a-Si:H FILMS WITH ONLY THE 2000-cm\(^{-1}\) IR ABSORPTION BAND


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ABSTRACT: The IR vibrational absorption spectra of a-Si:H films show two bands at 2000- and 2100-cm\(^{-1}\), attributed to SiH stretch vibrations. The widespread association of the 2000-cm\(^{-1}\) band with useful photoelectronic properties is tested. It is found that sputtered a-Si:H films deposited close to the target display only the 2000-cm\(^{-1}\) band, but these films also have much deteriorated properties. It is proposed that both results are caused by increased target-particle bombardment at close distances. Regardless of the mechanism involved, these results are presented as definitive evidence against the unique association of the 2000-cm\(^{-1}\) band with useful photoelectronic properties.

INTRODUCTION: Much consideration has been given to the relative intensities of the SiH vibrational absorption bands at 2000- and 2100-cm\(^{-1}\) in a-Si:H films. Based on the observation that the glow discharge films which have the best device properties show only the 2000-cm\(^{-1}\) band, and that sputtered films, which often have less desirable properties, usually have a dominant 2100-cm\(^{-1}\) band, a high 2000/2100 ratio has often been uniquely associated with high quality a-Si:H films. Consequently, elimination of the 2100-cm\(^{-1}\) band in sputtered a-Si:H has been sought and, indeed, films with only the 2000-cm\(^{-1}\) band have been reported. Noticeable is the fact, however, that none of these results was accompanied by reports of the expected improvements in photoelectronic properties. We have now carried out IR vibrational absorption, optical absorption, dark conductivity, photoconductivity, and photoluminescence measurements on a-Si:H samples produced by placing substrates at different positions in the sputtering plasma. We find that the ratio of the integrated intensities of the 2000- and 2100-cm\(^{-1}\) bands, A(2000)/A(2100), increases rapidly with decreasing target-substrate distance, with films closest to the target displaying essentially only the 2000-cm\(^{-1}\) band. We also find that films prepared close to the target have much deteriorated photoelectronic properties. We present these results as definitive evidence against the unique association of the 2000-cm\(^{-1}\) band with useful photoelectronic properties. We propose that the high A(2000)/A(2100) ratio is actually induced by target-particle bombardment, which at the same time is responsible for the inferior properties of these films.

EXPERIMENTAL: We made a series of depositions where substrates were placed on different height glass "pedestals" on the substrate platform of the RF sputtering system. With this arrangement we prepared a-Si:H films with different target-substrate separations simultaneously, and without changing the basic geometry of the plasma cavity. The substrate platform was kept at 200° C, but the temperature of the substrates on the pedestals was not controlled. Other parameters of the deposition were: RF power = 200 W; partial pressure of hydrogen = 0.8 mT and of argon = 5 mT.
Fig. 1: $E_{04}$, $E_g$, $I_{PL}$, $W_{PL}$, $(\mu\tau)_n$, $\sigma_{RT}$ and the ratios $A(2000)/A(\omega)$, $A(2100)/A(\omega)$, $A(2000)/A(2100)$ plotted vs. target-substrate distance.
RESULTS: Fig. 1 shows the parameters obtained from the characterizational measurements plotted vs. the target-substrate separation: \( E_{04} \), the energy at which the absorption coefficient \( \alpha \) equals \( 10^4 \text{ cm}^{-1} \); \( E_\sigma \), the conductivity activation energy; \( I_{PL} \), the relative photoluminescence intensity; \( W_{PL} \), the width of the photoluminescence peak; \( \sigma_{RT} \), the room temperature dark conductivity; \( (\mu \tau)_n \), the mobility-lifetime product for electrons derived from photoconductivity measurements; \( A(2000)/A(W) \), \( A(2100)/A(W) \), the integrated intensities of the 2000- and 2100-cm\(^{-1}\) bands normalized to the integrated intensity of the 640-cm\(^{-1}\) wag band, \( A(W) \), (assumed to be proportional to the total H content), and the \( A(2000)/A(2100) \) ratio. It is observed that \( E_{04} \), \( E_\sigma \), \( I_{PL} \) and \( (\mu \tau)_n \) decrease rapidly, after initial slight increases, as the target-substrate separation decreases, while \( W_{PL} \) and \( \sigma_{RT} \) increase. The IR parameters show monotonic changes with the target-substrate distance: \( A(2100)/A(W) \) vanishes for samples closest to the target and \( A(2000)/A(2100) \) increases significantly. The IR stretch bands of two films, one on the substrate platform and one 1 inch away from the target, are shown in Fig. 2.

DISCUSSION: From Fig. 1 it is seen that the decrease in the target-substrate separation leads to an increase in the \( A(2000)/A(2100) \) ratio which is paralleled by deterioration of the photoeletronic properties. The decreasing \( E_{04} \) indicates a narrowing gap, while the increasing \( W_{PL} \) suggests broadening band edges. The quenching of the photoluminescence, reduction of \( (\mu \tau)_n \), for electrons and the increase in the dark conductivity are all symptomatic of high defect concentrations and a large density of states in the gap in films deposited close to the target. It is essential to mention that the hydrogen content \( c_H \), drops from 14 at.% for samples on the substrate platform to 9 at.% for the ones closest to the target and this change in \( c_H \) is not sufficient to explain the observed changes in the properties.

It is known that secondary electrons and negative ions emitted from the target during sputtering can be accelerated to very high velocities as they fall through the dark space. These particles can bombard the growing film surface with considerable energies if the target-substrate distance is too small or the total
gas pressure is too low to allow thermalization before impact. We believe that this target-particle bombardment is the cause for the deterioration of the properties with decreasing target-substrate distance.

Based on the results of He\(^+\)-ion bombardment studies\(^6\) where it was shown that bombardment induced damage enhanced the intensities of certain IR bands, we conjecture that the elimination of the 2100-cm\(^{-1}\) band and the increase in the A(2000)/A(2100) ratio with decreasing target-substrate separation is also caused by increasing target-particle bombardment at closer distances. We suppose that the bombardment during the growth of the film promotes \(H\) incorporation into sites associated with the 2000-cm\(^{-1}\) band.

A close look at the sample preparation conditions in the reports on sputtered films with only the 2000-cm\(^{-1}\) band reveals that this was achieved through high RF power levels or by placing substrates a short distance away from the target, just outside the dark space\(^5\). Thus both methods seem to rely on increased target-particle bombardment for eliminating the 2100- bands.

Regardless of the exact mechanisms involved, however, the experimental observations of this study provide definitive evidence against the unique association of the 2000-cm\(^{-1}\) band with useful photoelectronic properties.

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References.
3. The calibration of the hydrogen content, \(c_H = N_H/(N_H+N_S)\times100\), to \(A(\omega)\) was deduced from a comparison of \(H\) evolution, nuclear reaction and IR measurements on sputter deposited films.
5. The initial increases in \(E_{\text{Oa}}, E_r, I_p\), and \(\mu\) can be explained in terms of slightly more favorable effective growth temperatures that these films, which are thermally isolated from the temperature controlled substrate platform, experience due to plasma heating.