Native Oxide Growth on Polycrystalline Undoped CdSeTe/CdTe Surfaces and Its Impact on Solar Cell Performance

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***Abstract* — Ambient air exposure between the absorber (CdTe) and back contact (Te layer) deposition was varied to control the native oxide formation on CdTe surface. A short air exposure period (~ 30 min) led to an improvement in open-circuit voltage (Voc) by 60 mV as compared to the device with minimal ambient air exposure, and enabled power conversion efficiency (PCE) reaching > 17.5 % in devices with no intentional doping (undoped). In contrast, 1-day exposure resulted in a kink in the J-V, indicating a barrier formation. X-ray Photoelectron Spectroscopy (XPS) analysis verified a native oxide formation on the absorber surface. One month air exposure post acid etch did not exhibit an s-kink in the J-V but severe kink was observed for unetched surface exposed under identical conditions. Notably, XPS analysis indicates an oxide layer on etched as well as unetched surface. This suggests that nature of the oxides formed on these surfaces may not be identical.**

Keywords: CdTe, Surface passivation, buffer-layer, native oxide, s-kink, chalcogenide, XPS

I. Introduction

As-deposited polycrystalline CdTe based films are typically subjected to $CdCl_2$ passivation treatment. Native oxide grows on CdTe surface during the ambient $CdCl_2$ treatment [1] or by simple air exposure [2] before the back contact deposition. Yi et al [2] showed that native oxide (TeO_2) of estimated thickness of 2 nm formed on chemical vapor deposition (CVD) grown polycrystalline CdTe surface after 6 months of air exposure, resulting in higher Voc. Similarly, Rugen-Hankey et al [3] showed that both aging and controlled annealing of metal-organic chemical vapor deposition (MOCVD) grown CdZnS/CdTe solar cell, improved the fill-factor (FF) and Voc, and attributed this to the formation of native oxide. In contrast, McCandless et al [1] reported that residual oxide phases ($CdTeO_3$ or CdO) formed on vapor transport (VT) grown CdTe during the $CdCl_2$ or heat treatments in air resulted in poor FF. Surface treatments are generally implemented to etch away such oxides formed on the CdTe surface [4,5]. Benefits of the native oxide, if there are any, are not well established/realized in polycrystalline CdSeTe/CdTe PV devices.

In this work, air exposure time between the absorber and back contact (Te layer) deposition is varied to allow the formation of native oxide and its effect on the JV characteristics are studied. X-ray photoelectron Spectroscopy (XPS) technique is used to analyze the CdTe surface.

II. Experimental detail

a) Absorber deposition

First, a 100-nm electron selective buffer layer, MZO, was RF sputtered on to a glass substrate coated with a 300 - 400 nm of fluorine doped tin oxide (FTO) coated by the manufacturer. This was then manually transferred to in-line multi-station thin film CdTe processing system, where a 400 – 600 nm of CdSeTe layer and 2.5 - 3.0 µm of CdTe layer was grown from a $CdSe_{0.4}Te_{0.6}$ and CdTe source material respectively, via closed-space sublimation process. Followed by a vacuum $CdCl_2$ treatment since it mitigates the formation of native oxide which otherwise reported to form during an atmospheric $CdCl_2$ treatment. The residual $CdCl_2$ haze deposited on the film was then rinsed off using deionized water and dried under argon flow

b) Air exposure and acid etch

Various substrates with different air exposure duration and acid etch configurations were produced as described in detail below:

(i) Absorbers were exposed to the lab air for 6 min, 30 minutes, 3 hrs and 1 day before the back contact deposition (Fig 1. a).
(ii) Absorber was acid etched after 1 day of exposure before the back contact deposition (Fig 1. b).
(iii) Absorber was acid etched prior to 1 day of air exposure before the back contact deposition (Fig 1. c).

For acid etching, a solution of 5% v/v of diluted hydrochloric (HCL) acid solution was used. Films were dipped in the solution for 12 sec followed by rinsing with Isopropanol and Deionized water.

c) Back contact deposition

Post air exposure or acid etch treatments, 35 - 45 nm of Te was evaporated on to all the substrates, followed by spraying C and Ni paint to act as back electrode.

All the samples compared were fabricated in the same batch and duplicates of few variants were produced to ensure the variations observed were statistically relevant (Fig 1S).

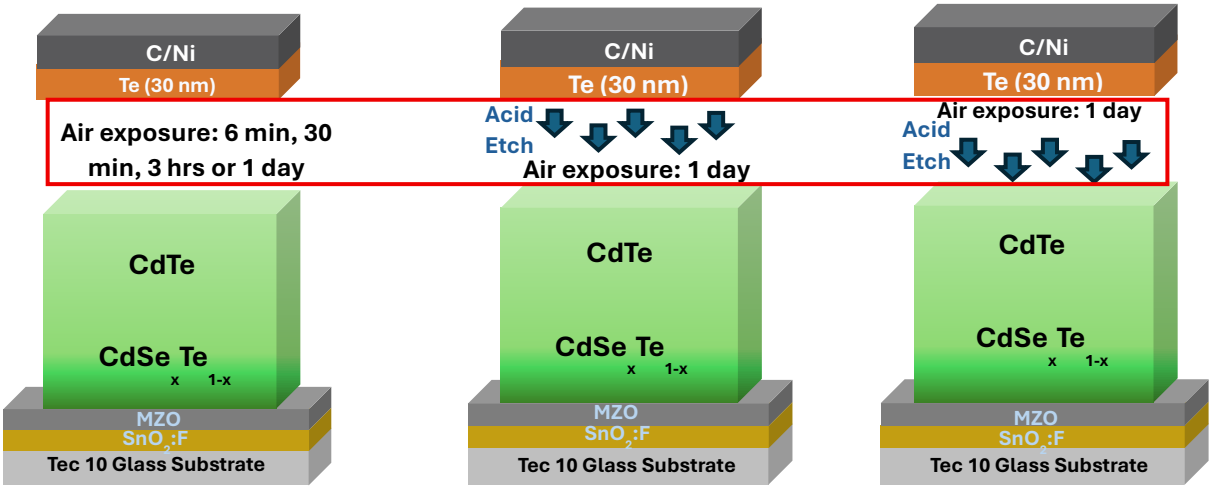

Fig 1. Device structure of a) varied air exposure time (6 min, 30 min, 3 hrs or 1 day) CdTe and back contact (Te) deposition; b) acid etch performed post 1 day air exposure c) acid etch prior to 1 day air exposure

III. RESULTS AND DISCUSSION

A. CdTe Surface Analysis – XPS

X-ray photoelectron spectroscopy (XPS) surface analysis was performed on CdTe sample after 3 hours of ambient air exposure. This exposure duration was chosen due to logistical constraints as minimum transfer time of approximately 40 minutes was required between fabrication laboratory and loading into XPS intro chamber.

The survey scan of CdTe surface (Fig 2.) shows core-level binding energies corresponding to Cd (3p and 3d), Te (3p and 3d), O 1s and C 1s (arising from surface carbonaceous contamination). Due to high signal intensity, 3d core levels are generally selected for high-resolution XPS scans. The Te 3d and Cd 3d core level exhibit two spin orbit components $3d_{5/2}$ and $3d_{3/2}$. All the binding energies were calibrated with respect to the Cd $3d_{5/2}$ (Cd-Te) binding energy. The Te $3d_{5/2}$ exhibits two components, corresponds to Te^{2-} and Te^{4+} states (Fig 3 b). The lower binding energy peak (Te^{2-}) at 572.5 eV corresponds to Te-Cd bonding, while the higher binding energy peak (Te^{4+}) at 576.1 eV is associated with Te-O bonding, confirming the formation of a native oxide on the CdTe surface.

Similar oxide related peak (Te - O) have been reported in CdTe film following ambient heat annealing [3], prolonged air exposure [6] or rapid post-annealing oxidation [7]. In contrast, the Cd $3d_{5/2}$ exhibit a single dominated Cd^{2+} peak (Fig 3. a). Since the binding energies of Cd-Te and Cd-O are very close (< 1 eV) [8,9], it is challenging to conclusively distinguish between mixed oxide ($CdTeO_x$) or tellurium oxides (TeO_x), particularly in polycrystalline films.

Historically, there have been conflicting reports regarding the composition of native oxide on CdTe surfaces. Transmission electron microscopy (TEM) study establishes the formation of epitaxial TeO_2 formed on single crystal CdTe surface post bromine – methanol etch and air exposure [10]. Some XPS and AES studies identify it as mixed oxide ($CdTeO_x$) [9] while others conclude as TeO_2 [2,11]. In contrast, glancing incidence X-ray diffraction (GIXRD) analysis concludes the formation of $CdTeO_3$ on CdTe surface after heat treatments in air [1].

The ambiguity in oxide identification through XPS analysis arises from attributing the additional Te $3d_{5/2}$ peak exclusively to TeO_2, particularly in the absence of a distinct Cd-O peak. However, as discussed earlier, the binding energies of Cd-O and Cd-Te are very similar making it challenging to conclusively rule out mixed oxide formation. The TEM study [10] mentioned earlier involved surface etching, which likely produced a Te rich surface and consequently favored the formation of TeO_2, as reported in that study.

In section C, the CdTe surface was modified by acid etching followed by air exposure to form a native oxide. Consequently, the nature of the native oxides formed with and without acid etching was inferred from the corresponding J-V behavior.

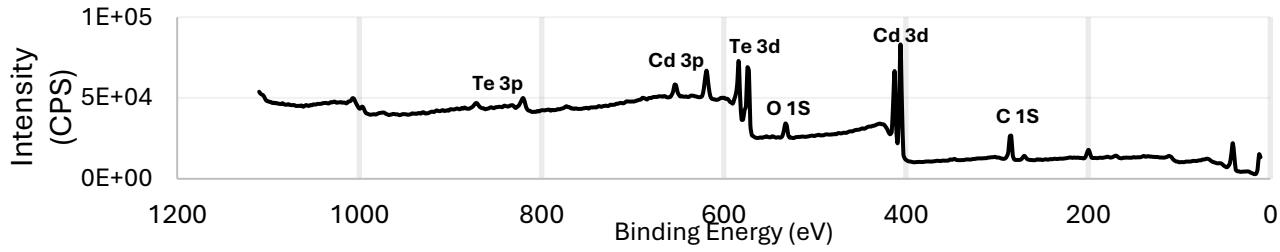

Fig 2. X-ray photoelectron spectroscopy (XPS) survey scan of CdTe surface post 3 hours of air exposure

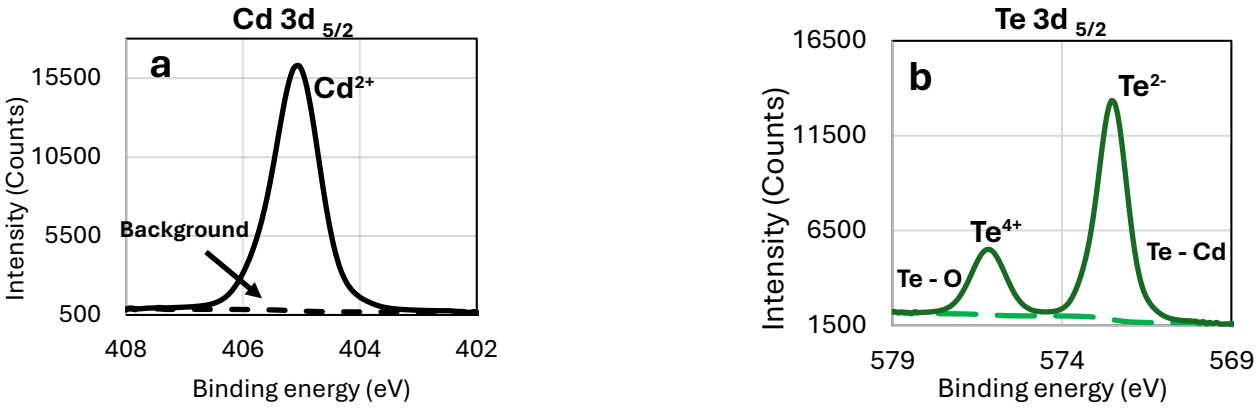

Fig 3. XPS spectrum of core levels of a. Cd $3d_{5/2}$ and b. Te $3d_{5/2}$

B. Device Performance (no intentional doping step)

Air exposure time between absorber (CdTe) deposition and back-contact (Te layer) deposition was varied to allow the growth of native oxide on CdTe surface (Fig 1. a). A 6 min air exposure time between the absorber and back contact deposition resulted in highest FF > 75 % (Fig 6.c). increasing the exposure time to 30 min led to an improvement in Voc by more than 60 mV (fig 6.a) (comparing median cells). This enhancement in Voc is attributed to native oxide formation, which likely passivates surface dangling bonds on CdTe. However, prolonging air exposure to 1-day resulted in a s-kink in the J-V (Fig 6). Consequently, FF decreased from 71.7% to 48% as the air exposure time increased from 30-min to 1-day (Fig 7.c). This degradation is likely due to further oxide growth which acts as hole barrier at the back of the device. This demonstrates that the duration of air exposure is critical for achieving beneficial surface passivation while minimizing the adverse effects on the FF.

Acid etching is known to remove the oxide from the CdTe surface [11]. Consequently, acid etch after 1 day air exposure restored the J-V characteristics and mitigated s-kink (Fig 6.). As a result, FF improved from 48% to 72%, confirming that the s-kink is due to the formation of native oxide due to prolonged air exposure, which introduces a barrier to hole transport at the back contact. However, significant Voc loss was observed upon acid etching either due to removal of favorable native oxide species or as detrimental effect from preferential etching at grain boundaries as shown by Misra, S. et al [12]. Reese, M. et al [13], reported Te rich surface is prone to high recombination. However, 1-day air exposure post acid etching improved the Voc from 590 mV to 654 mV, likely due to regrowth of favorable native oxide (Fig 6 and Fig 7.c). In contrast, FF reduced to 63.2 %, better than 1 day air exposure in the case of the unetched sample where the FF went to 48%. Presently, it is unknown if the increased air exposure (> 1 day) post acid etch further improves the Voc.

Capacitance-Voltage (C-V) and temperature dependent J-V (J-V-T) measurements were performed on 6 min and 30 min air exposure. The net carrier concentration as a function of depletion width (distance from the junction) for both 6 min and 30 min were found to be nearly identical as shown in Fig 4.a – indicating that the observed gain in Voc is not due to changes in bulk doping. In addition, activation energy (E_a) was extracted from the J-V-T measurement by linearly extrapolating the of the V_{oc}-T relationship to 0K. The E_a was higher in 30 min air exposure compared to 6 min (Fig 5), suggesting reduced recombination losses. This supports the surface passivation effect of native oxide that led to improved Voc.

Overall, short air exposure improved the Voc in undoped CdSeTe/CdTe PV devices with small impact on the FF, leading to an improved PCE. However, longer exposure resulted in s-kink in the JV due to the formation of hole barrier.

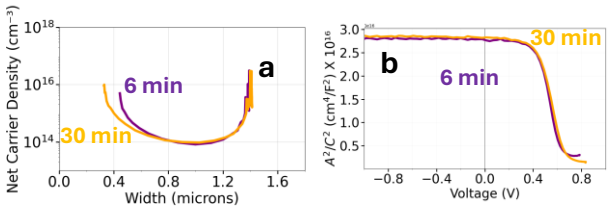

Fig 4. a. Net carrier concentration Vs width, b. Mott-stocky plot comparison between samples with 6 minutes and 30 minutes air exposure

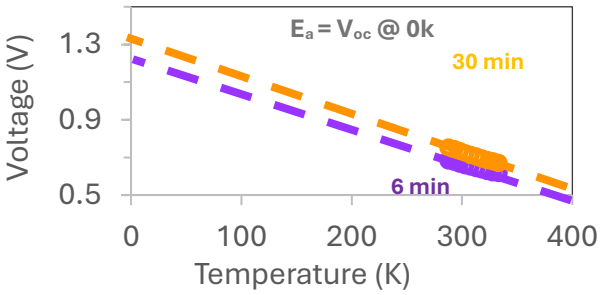

Fig 5. Temperature -Voltage plot comparison between samples with 6 min and 30 minutes air exposure

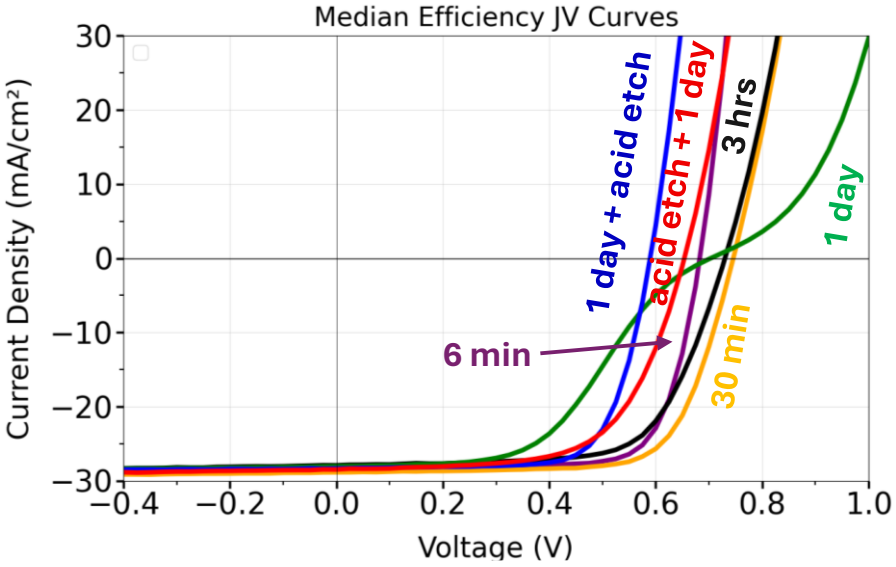

Fig 6. Current density – Voltage (J-V) characteristics of median cells in Fig 7.

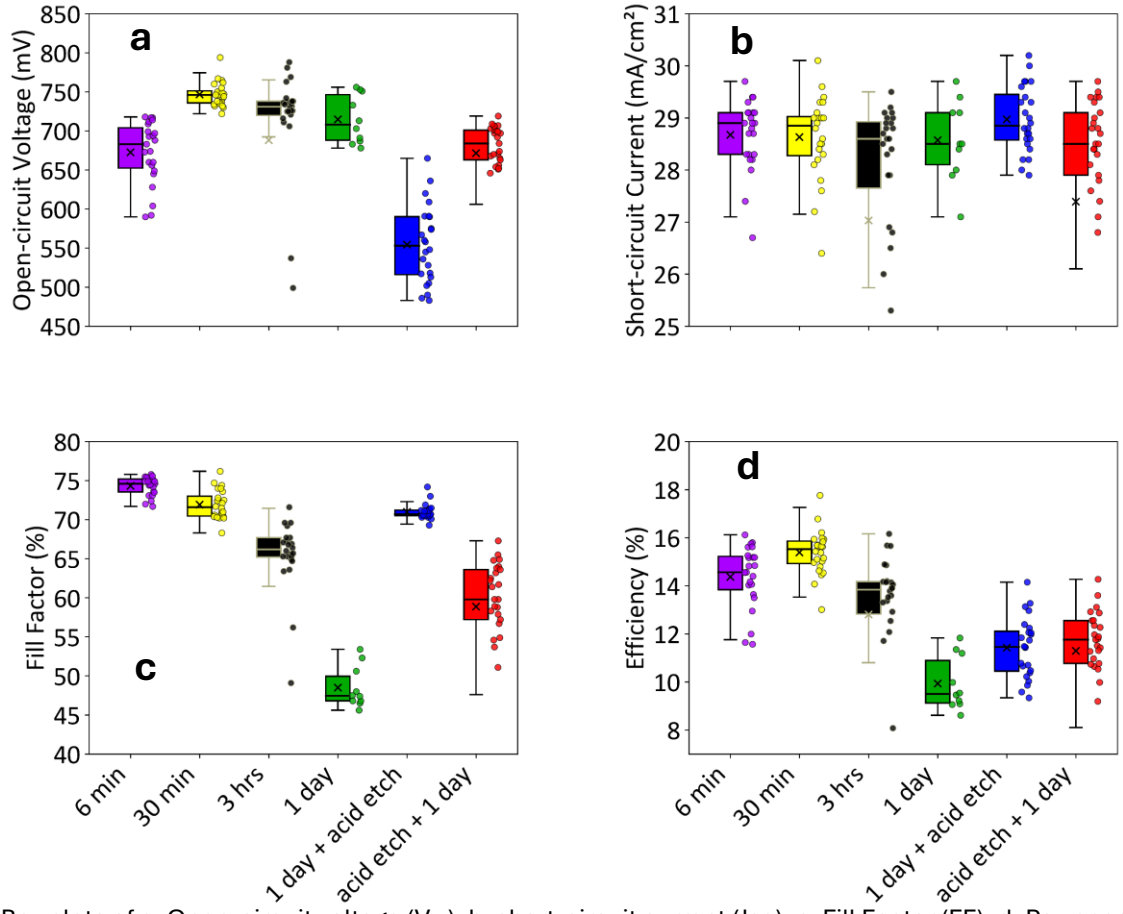

Fig 7. Box plots of a. Open-circuit voltage (V_{oc}); b. short-circuit current (Jsc); c. Fill Factor (FF); d. Power conversion efficiency (PCE) of samples with varied air exposure time (6 min, 30 min, 3 hrs or 1 day) between CdTe and back contact (Te) deposition; acid etch performed post 1 day air exposure; acid etch prior to 1 day air exposure

C. Extended Air Exposure Post Surface Modification

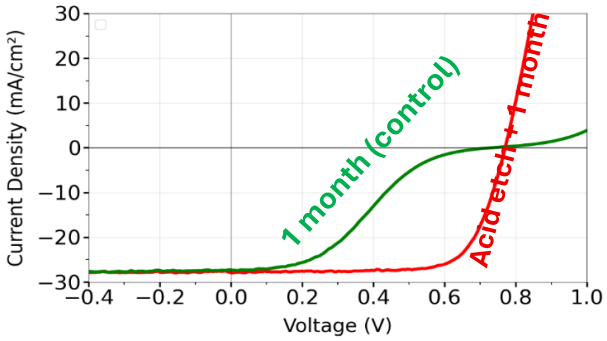

Fig 8. J-V comparison of sample with and without acid etch prior to 1-month dry-air exposure

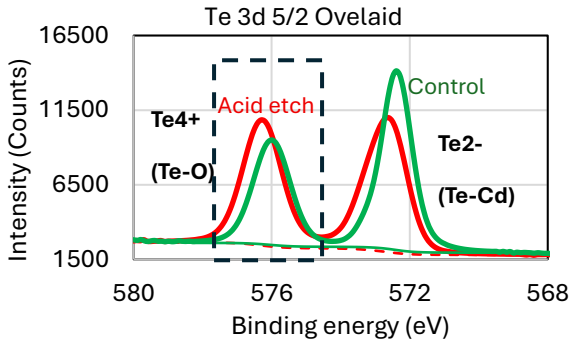

Fig 9. XPS measurement of etched vs unetched samples after about 1-month dry-air exposure

As discussed earlier, 1-day air exposure resulted in s-kink whereas 1-day air exposure post acid etch did not cause any s-kink (Fig 6). To further investigate this effect, CdTe surface was treated with comparatively higher concentrated (10% v/v) HCL solution for 12 sec. Both the acid etched sample and a control (no acid etch) were stored in dry-air (inside an airtight container with desiccant to minimize the effect of moisture) for a month to allow the formation of native oxide on CdTe surface prior to the back contact deposition. Despite identical exposure conditions and duration, the control sample exhibited s-kink, whereas acid etch sample showed a good J-V behavior (Fig 8 and Fig 2S). Interestingly, XPS performed on films treated and stored under similar conditions revealed a stronger oxide peak (Te-O) on acid etch sample compared to control (Fig 9).

Despite having an oxide overlayer on both control and etched sample, J-V indicates a barrier formation in case of control but not in the acid etch sample. This suggests that the chemical nature of the native oxide that forms on the acid etched film is different from the unetched sample. A recent XPS study [14] reports mixed oxide ($CdTeO_x$) formation on CdTe surface with no surface treatments. Further XPS analysis is required to determine the composition of the oxide formed on the acid etched sample.

IV. CONCLUSIONS

Overall, the extended air exposure (30-min, 3-hrs and 1-day) samples exhibit higher Voc but lower FF than the 6-min sample. Due to a higher gain in the Voc than the loss in the FF, 30-min air exposure enabled highest PCE reaching > 17.5 % - highest performing absorber without any intentional doping step. The 1-day wait sample exhibited s-kink in the J-V. Native oxide likely helps in improvement of Voc in undoped devices; however, longer exposure is affecting the FF.

Acid etching the CdTe surface after a 1-day wait did not result in the s-kink, likely due to removal of native oxide. Acid etching resulted in poor Voc, likely due to removal of passivating oxide and creation of additional non-radiative recombination channels. However, Voc recovered after 1-day air exposure post acid etching – likely due to growth of favorable native oxide, with a drop in the FF – not a significant drop like seen in unetched case after 1-day wait.

The 1-month dry-air exposure post acid etch (10% v/v HCL) showed good diode behavior, whereas control (unetched) exhibited s-kink in the J-V. XPS measurement reveals surface oxide in both the cases, these oxides likely have different characteristics since the devices have completely different J-V behavior. Further XPS depth profiling study is required to determine the chemical compositions of the native oxides.

Based on the J-V characteristics, air exposure of both unetched and acid etched CdTe surface led to an improvement in Voc. However, the native oxide formed on the unetched CdTe surface likely exhibits an unfavorable band alignment, whereas the oxide formed on the etched surface is expected to have a more favorable valance band alignment with CdTe. Further studies are required to elucidate the band alignment of these oxides with CdTe, the kinetics of oxide growth with and without etching [15], and the influence of environmental factors such as moisture during the oxide growth [16] on solar cell performance.

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Supplementary

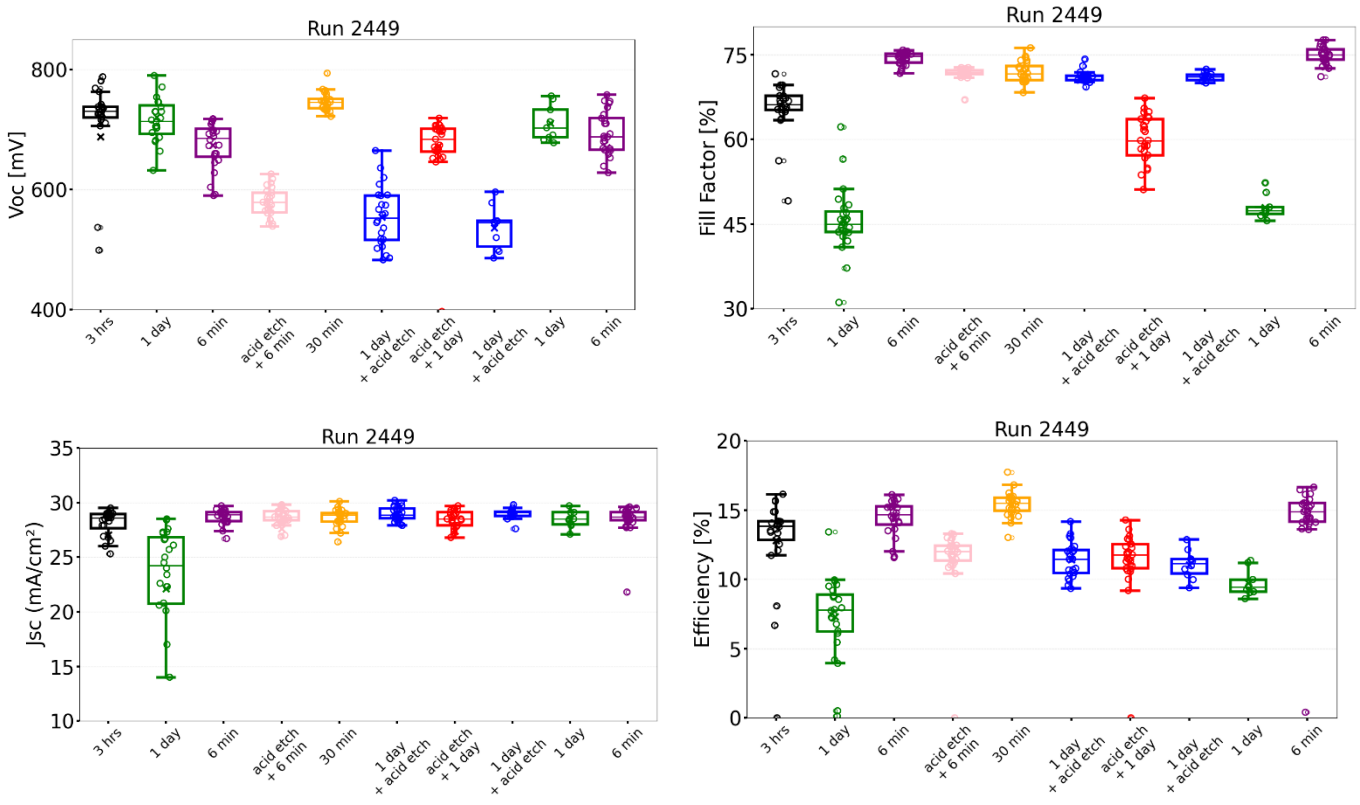

Fig S1: Duplicate devices were included for few variants to verify that the observed variations were statistically significant. The box plots are presented in the order in which the devices were fabricated.

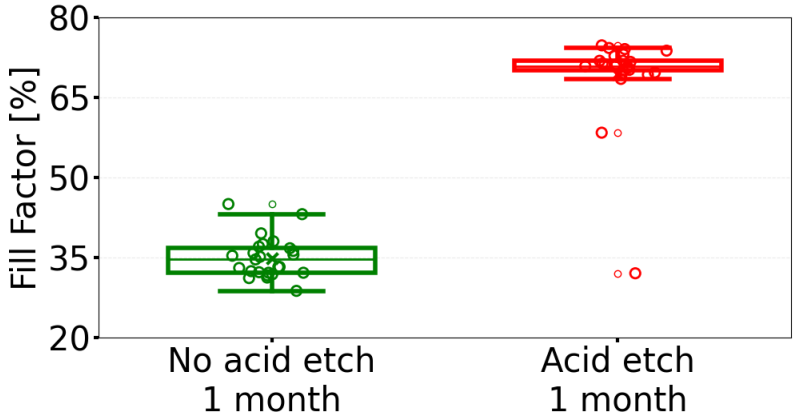

Fig S2: Fill-factor comparison of 1 month dry-air exposure with and without acid etch.