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Influence of light, heat and humidity on MAPbI$_3$/Si interface stability

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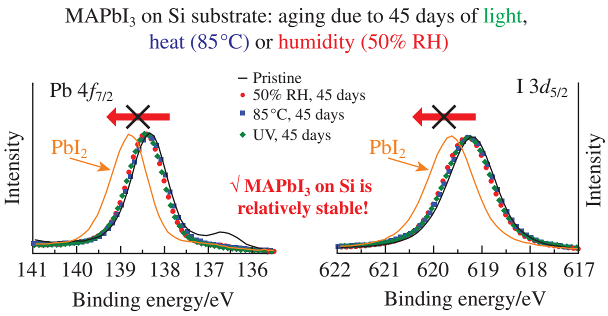
X-ray photoelectron spectroscopy (XPS) was used to examine the MAPbI$_3$/Si interface (MA = methylammonium) before and after 45 days of exposure to light, heat stress at 85 °C or 50% relative humidity (RH). From the survey XPS spectra it follows that under these external influences, changes in the I/Pb ratio, indicating the presence of the PbI$_2$ phase as a degradation product, do not go beyond 12%. These results were confirmed by measurements of high-resolution XPS spectra in the energy ranges of Pb 4*f*, I 3*d* and valence band signals, which do not show significant high-energy shifts towards the energy position of the PbI$_2$ reference spectra.



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Despite the active search for cheaper alternatives, silicon solar cells still dominate industrial photovoltaics with a market share of over 90%[1] and are expected to remain the leaders in photovoltaic technology. This is due, first of all, to the high resistance of silicon solar cells to external influences, which ensures their long service life. On the other hand, their state-of-the-art power conversion efficiency reaches 26.7%,[2] approaching its theoretical limit of 29.4%.[3] It should be noted that a fundamental limitation to the efficiency of silicon solar cells is that c-Si has a band gap of 1.12 eV, which prevents the absorption of high-energy photons. One of the widely discussed ways to solve this problem[4–12] is to create a tandem of silicon with a hybrid perovskite that has a larger band gap (from 1.6 to 1.9 eV).[13] Evaporation techniques make hybrid perovskite a suitable candidate for the perovskite/Si tandem configuration. When a hybrid perovskite is deposited on crystalline silicon, its 1.6 eV band gap will absorb high-energy photons, while c-Si with a 1.12 eV band gap will be responsible for absorbing low-energy photons. If the MAPbI$_3$/Si tandem is implemented by combining silicon and perovskite-based solar cells, then direct deposition of a perovskite layer on silicon nanostructures can be used to create efficient light-emitting diodes[14] and photodetectors.[15] The paper[16] reports on a light-emitting diode based on a halide perovskite deposited on top of a p-type silicon substrate, which serves to introduce holes into the perovskite. A necessary condition for using a hybrid perovskite/silicon interface is to increase the resistance of perovskite materials to external influences, which should reach values comparable to silicon technologies. Despite the great interest in this problem, research into the photochemical and thermal stability of perovskite/Si interfaces, as well as resistance to relative humidity, is still just beginning.[17,18] The article[19] deals with the study of perovskites under the influence of heat and light (not UV) for samples deposited on an inert substrate (silica glass). Such an inert substrate makes it possible to study the intrinsic degradation mechanisms of perovskite, but is not used in practical applications. At the same time, the influence of various interfaces on the stability of MAPbI$_3$ is widely known. Thus, the main goal of this work was to demonstrate the remarkable stability of the MAPbI$_3$/Si interface to various influences. We present the results of an X-ray photoelectron spectroscopy (XPS) study of a MAPbI$_3$/Si interface[†] that was irradiated with UV light, annealed at 85 °C or exposed to 50% relative humidity for 45 days.

The use of a full set of XPS spectra, including a survey spectrum, core-level and valence band (VB) spectra, allows one to obtain unique information on the composition, chemical bonding and electronic structure of hybrid perovskites, as well as on the change in these characteristics with exposure time.[19,20]

[†] After several years of development, the preparation of MAPbI$_3$ thin films has been optimized for the production of high-efficiency perovskite solar cells.[21,22] By forming adducts with solvent molecules such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), and through antisolvent engineering, perovskite thin films with high crystallinity and large grain sizes have been successfully prepared using a simple solution spin-coating process.[23] In this work, we selected a widely used perovskite precursor recipe and then used a two-step annealing process with optimized annealing temperature to obtain MAPbI$_3$ films with high crystallinity and large grains. Detailed optimization of fabrication method parameters, including annealing temperature,[24] two-step annealing process,[21–23,25] and adduct precursor with antisolvent step,[23] can be found in the cited papers. In addition, relevant

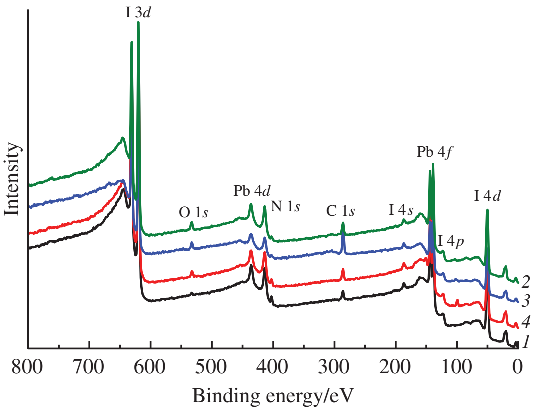

Figure 1 Survey XPS spectra of the $MAPbI_3$/Si interface (*1*) before and after 45 days of exposure to (*2*) light, (*3*) heat stress at 85 °C or (*4*) 50% RH.

As follows from the survey spectra shown in Figure 1 and quantitative data on the surface composition (Table 1), the studied samples did not contain uncontrolled impurities. Note that some silicon contribution can be seen in degraded samples, indicating film thinning. We have not labeled the Si 2*p* peak in the figure so as not to clutter the spectra with labels. However, a peak around 99 eV is clearly observed in samples after exposure to moisture (Figure 1, curve *4*). Also noteworthy is the relatively low oxygen content, which makes it possible to exclude oxidation of the samples during the aging process. Of particular interest is also the I/Pb ratio, which should decrease in the case of release of the PbI_2 phase as a degradation product caused by external influences. In this regard, from the surface compositions it follows that the decrease in this ratio upon heating or irradiation does not exceed 12%, which indicates sufficient resistance of the $MAPbI_3$/Si to these influences.

Table 1 Surface composition of the $MAPbI_3$/Si tandem before and after aging.

Sample history	C (at%)	O (at%)	N (at%)	Pb (at%)	I (at%)	Si (at%)	I/Pb
As prepared	33.8	2.7	13.6	14.6	35.3	–	2.41
50% RH, 45 days	33.6	7.7	8.0	11.0	26.3	13.4	2.39
85 °C, 45 days	67.9	6.2	3.3	6.1	13.1	3.4	2.14
UV, 45 days	42.2	9.9	6.4	12.3	26.4	2.8	2.14

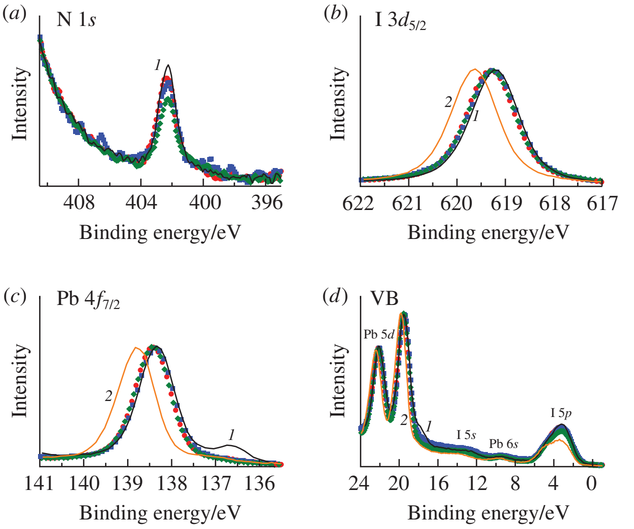

Figure 2 High-resolution XPS spectra in the energy ranges of (*a*) N 1*s*, (*b*) I 3*d*, (*c*) Pb 4*f* and (*d*) VB signals for (*1*) the initial $MAPbI_3$/Si interface and the same after 45 days of exposure to light (◆), heat stress at 85 °C (■) or 50% RH (●) compared to (*2*) the reference compound PbI_2.

The ability to selectively excite the X-ray spectra of $MAPbI_3$/Si components and the high sensitivity of these spectra to the immediate environment of excited atoms makes it possible to obtain unique information about the local atomic and electronic structure of perovskites exposed to heat, light or humidity. Measurements of N 1*s* spectra normalized to the intensity of the Pb 4*d* line [Figure 2(*a*)] showed that under these influences the relative intensity of these spectra decreases only slightly, which indicates the relative stability of the C–N bonds in the MA cation. As our previous studies[20] have shown, the Pb 4*f* and I 3*d* spectra of the reference compound PbI_2 demonstrate a high-energy shift of the order of 0.5 eV relative to $MAPbI_3$, which makes it possible to detect even partial separation of the PbI_2 phase as a degradation product. The results presented in Figure 2(*b*),(*c*) show no noticeable changes compared to the spectra of the initial $MAPbI_3$/Si interface, which practically excludes separation of the PbI_2 phase as a result of degradation. Independent information about the separation of the PbI_2 phase can be obtained from measurements of VB spectra. As follows from our previous measurements,[19,20] the relative intensity of these spectra, normalized to the intensity of the Pb 5*d* spectrum, is much lower than that of the initial $MAPbI_3$ perovskite. From the measurements of the VB spectra presented in Figure 2(*d*), it can be concluded that the separation of the PbI_2 phase as a degradation product of the $MAPbI_3$/Si interface is very insignificant.

The development of halide perovskite materials on the silicon optoelectronics platform is an important step for the practical implementation of optoelectronic devices. In this regard, the characterization of halide perovskites integrated with silicon and exposed to external influences at the atomic and electronic levels is of not only fundamental, but also practical interest. In this work, based on measurements of XPS spectra of core levels of component atoms and VBs, it is shown that $MAPbI_3$/Si interfaces are sufficiently resistant to light, heat and humidity and can be used for practical applications.

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properties of $MAPbI_3$ thin films prepared using the same fabrication method can be found in our previous work. The UV-VIS absorption and XRD peaks show that the $MAPbI_3$ films have high coverage and crystallinity.[26] Briefly,[27], equimolar amounts of PbI_2 and MA iodide were dissolved in DMF–DMSO (8.9 : 1.1, v/v) to form a 1.5 M solution of the $MAPbI_3$ perovskite precursor. The Si substrates were first treated with air plasma for 10 min to remove unwanted residues and increase surface hydrophilicity. Then, the precursor solution was spin-coated at 4000 rpm for 20 s, and the antisolvent diethyl ether was dripped onto the substrate after 7 s of spin-coating process, followed by thermal annealing at 60 °C for 1 min and at 100 °C for 30 min.

XPS was used to measure core-level and VB spectra of $MAPbI_3$/Si interface samples on a ULVAC-Physical Electronics PHI XPS 5000 VersaProbe spectrometer. The energy resolution was $\Delta E \leqslant 0.5$ eV for Al Kα X-ray emission. $MAPbI_3$ perovskite films were prepared using a one-step spin-coating strategy with an antisolvent dripping step.

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