Doped Nickel Oxide Carrier-Selective Contact for Silicon Solar Cells

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Abstract—Transition metal oxides such as MoO$_3$, WO$_3$, V$_2$O$_5$, and NiO have shown potential as hole-selective passivating contact for crystalline silicon (c-Si) solar cells. Among them, NiO is a notoriously poor hole-conducting semiconductor. Doping metal oxide with multivalent metal cations is an effective method to modify their electronic properties because dopant-induced favorable defect states play a crucial role in charge carrier transport in device applications. We use first-principles density functional theory to identify suitable metal cations that favorably affect the hole-conducting properties of NiO. We identify Al, Mg, and Zn as suitable dopants for NiO, improving ohmic contact properties with c-Si. Subsequently, Al-doped NiO (Al$_x$Ni$_{1-x}$O) films were synthesized onto c-Si using an atomic layer deposition supercycle approach. The Al$_x$Ni$_{1-x}$O films showed a contact resistivity of 331 m$\Omega$ cm$^2$ with c-Si, in contrast to undoped NiO where no ohmic contact could be formed. This in-depth computational study followed by the experimental synthesis of Al$_x$Ni$_{1-x}$O films removes a critical barrier for the future applications of NiO-based carrier-selective passivating contacts for c-Si and other types of solar cells and provides a path for the optimization of other functional materials.

Index Terms—Density functional theory (DFT), density of states (DOS), nickel oxide (NiO), passivation contact, p-type conductivity, Si photovoltaics.

I. INTRODUCTION

Transition metal oxides (TMOs) are low-cost, earth-abundant semiconducting materials, which are important for a wide range of applications, such as water splitting [1], gas sensing [2], solar cells [3]–[7], electrocatalysis [8], energy storage [9], and electrochromic displays [10]. TMOs may contain inherent, intrinsic vacancies and interstitial defects and extrinsic impurity-related defects, which significantly affect their electronic and optical properties. Therefore, extensive efforts have been taken to study defects in the TMOs to identify favorable combinations of defects and impurities that can significantly improve the final device performance. TMOs with a large work function and shallow defect states close to their conduction band (CB) or valence band (VB) are needed for an efficient collection of photogenerated charge carriers from crystalline silicon (c-Si). For NiO, shallow defect states at the VB are required as it is an appealing hole-collector due to its small band offset with the c-Si VB [11].

Stoichiometric NiO is a Mott-Hubbard insulator [12] with an extremely low electrical conductivity (<10$^{-13}$ $\Omega$ cm$^{-1}$) at room temperature [13]. However, a typical NiO film is non-stoichiometric and contains nickel vacancies (V$_{Ni}$), which are charge compensated by holes localized at Ni sites (Ni$^{2+}$) when the film is grown in excess oxygen conditions. These intrinsic defects make NiO a p-type semiconducting material with a hole mobility of 1.15 × 10$^{-3}$ m$^2$ V$^{-1}$s$^{-1}$ [14]. The reasonable hole conductivity combined with a relatively large bandgap of 3.4–4 eV [3] makes NiO a favorable hole-transporting material for perovskite [6], [15], quantum-dot [7], and silicon solar cells [4]. However, both a poor material conductivity plus intricate defect chemistry at the NiO/c-Si interface limit the power conversion efficiency of NiO-based silicon solar cells.

It is well known that the incorporation of extrinsic defects can change the electronic properties of semiconductors. It has been shown that substitutional Li, Na, and K on Ni-sites significantly increase the hole concentration in NiO as all of these atoms are monovalent in contrast to Ni, which is typically divalent. In the case of Li, which has a similar ionic radius (0.76 Å) compared with Ni$^{2+}$ (0.69 Å), the increased concentration of trivalent Ni thereby further enhances the NiO p-type conductivity (up to 11.2 S cm$^{-1}$), work function (up to 5.04 eV) as well as the hole concentrations (up to 6.13 × 10$^{21}$) [16]. However, Li-doped NiO is shown to have a low charge carrier mobility of 5 × 10$^{-3}$ m$^2$ V$^{-1}$s$^{-1}$ [16] and its integration in an n-type c-Si heterojunction solar cell only resulted in a modest champion efficiency of 6.3% [17]. Incorporation of Na and K improves the p-type conductivity of NiO film with resistivity values of 11.57 Ω cm and 23.7 Ω cm, respectively, along with high transparency in the visible light region of the solar spectrum and an increased carrier...
concentration of $3 \times 10^{16} - 7.18 \times 10^{19}$ cm$^{-3}$ compared with undoped NiO films [18], [19]. However, the carrier mobility of the K-doped NiO films is affected by the relatively large ionic radii of K$^+$ (1.3 Å) compared with Ni$^{2+}$ (0.69 Å). Despite the enhancement of electrical properties, the use of alkaline metal dopants in solar cells has not yet been reported.

The incorporation of Cu, Zn, and Al into the NiO$_x$ has been reported to enhance carrier concentration and consequently the electrical conductivity of NiO [4], [20]. A significant increase of carrier concentration and bandgap narrowing were reported for sputtered Al-doped NiO (Al$_2$NiO$_3$) films by Nandy et al. [21]; however, a theoretical study is needed to better understand the doped material. Yang et al. [4] showed that doping of NiO with Cu increased its work function from 4.34 eV for pure NiO to 4.58 eV, its carrier concentrations up to $1 \times 10^{19}$ cm$^{-3}$, and conductivity up to $\sim$50 S cm$^{-1}$ for 27.1 at% Cu-doped NiO. Silicon solar cells with a Cu-doped NiO hole collector had a significantly lower series resistance ($R_s$) and saturation current density ($J_0$) than their counterparts without undoped NiO resulting in a champion efficiency of 9.1% [4]. These promising results suggest that even though various groups have successfully altered the electronic properties of NiO, there is still room for improvement to reach its full potential in c-Si solar cells. We recently demonstrated a thermally stable Zn-doped NiO film with a low contact resistance of $\sim$20 mΩ cm$^2$ on c-Si, thus showing NiO’s potential as hole-contacts for c-Si solar cells [22].

NiO with an enhanced hole-conductivity and narrow VB offset with p-Si is needed to improve carrier separation and collection efficiency of NiO/c-Si heterojunction solar cells. First-principles density functional theory (DFT) calculations, a reliable theoretical tool that complements experiments by materials properties prediction, were carried out to identify potential dopants for increasing the conductivity of NiO. In this work, we first present DFT calculations of NiO host lattice with extrinsic W, Ta, Nb, Mo, Si, Sn, Ti, Sr, Zn, Al, Mg, and Hf dopants with a particular focus on their solubility and their effect on the electronic and optical properties. We show that these metal dopants can change oxidation states with respect to the host metal cation (Ni$^{2+}$) of NiO and Fermi level-dependent electronic properties of the doped NiO. To the best of our knowledge, a systematic DFT defect study on NiO doping has not been reported to date. Subsequently, Al$_2$NiO$_3$ films were synthesized onto c-Si using an atomic layer deposition (ALD) supercycle approach. The Al$_2$NiO$_3$ films were found to have a low contact resistivity on c-Si contact in good agreement with the DFT calculations.

II. METHODOLOGY

A. Computational Details

The computational work was carried out by the first-principles DFT approach using the projector augmented wave (PAW) [23] pseudopotentials as implemented in the Vienna Ab-initio Simulation Package [24]. For each element considered in this study, the number of valence electrons in the pseudopotentials is shown in parentheses: Ni (10), O (6), Zn (12), Al (3), Hf (12), Mg (8), Mo (12), W (12), Nb (13), Si (4), Sn (14), Sr (10), Ta (11), and Ti (12). The interaction between the valence electrons was first described by the generalized gradient approximation (GGA) as formulated in the Perdew-Burke-Ernzerhof (PBE) density functional [24], and selected calculations were repeated with the hybrid functional of Heyd–Scuseria–Ernzerhof (HSE06) [25]. A kinetic energy cutoff of 520 eV was used throughout. This yielded a total energy convergence within 1 meV, consistent with previous work on TMOs [22], [26], [27]. Integration over the Brillouin zone for the $2 \times 2 \times 2$ NiO supercell (64 atoms) was performed using a $5 \times 5 \times 5$ $k$-point mesh generated within the Monkhorst-Pack scheme, with Gaussian smearing of 0.01 eV [28]. The electronic density of states (DOS) was computed using the tetrahedron scheme, and all calculations were spin-polarized because of the antiferromagnetic (AFM) structure of the bulk NiO [29]. The rotationally invariant on-site Coulomb correction (GGA+U) was applied to the Ni 3d orbital using Dudarev’s formalism [30] with a U value of 5.3 eV, in line with published values [31].

Intrinsic vacancies of nickel ($V_{Ni}$) and oxygen ($V_{O}$) and substitutional extrinsic dopants were considered. The defectless supercell was fully relaxed (lattice parameters and atomic positions) until the energy difference between ionic steps was below $1 \times 10^{-6}$ eV, and forces on all ions were less than 1 meV/Å. The electronic convergence criteria were set to $1 \times 10^{-8}$ eV. Defect calculations were performed at a constant volume (only atomic positions were relaxed) to emulate better dilute conditions. As shown in Table I, most previous DFT studies used 32–128 atoms NiO supercells, where the choice of exchange-correlation functionals and $k$-points sampling were varied. Therefore, the suitability of the chosen supercell size for modeling point defects was verified by comparing the formation energy of Al$_{Ni}$ defects (charged and charge-neutral) obtained from the 64-atom supercell with those of the 512-atoms NiO supercells. As shown in Table II, the difference of formation energy among these supercells was reasonably small, confirming that the 64-atom supercells were adequate [32]. This was a necessary compromise in computational intensity to investigate
the large set of dopants considered here in the various charge states.

The formation energy $E_f^f(D_{Ni}^q)$ of charged intrinsic and extrinsic defects in NiO were calculated following (1) [26], [27], [37]

$$E_f^f(D_{Ni}^q) = E_{tot}^f(q) - E_{tot}^{host} + \sum n_i \mu_i + q (E_{VBMB} + \mu_e) + \Delta \varepsilon$$

where $E_{tot}^f(q)$ represents the total energy of a defect containing NiO supercell with charge $q$, $E_{tot}^{host}$ is the energy of a perfect NiO supercell of the same size, $n_i$ and $\mu_i$ are the number of atoms of a species $i$ removed from or added to the supercell, and the corresponding chemical potential of the atom, respectively. The electron chemical potential ($\mu_e$) represents the Fermi level referenced to the VB maximum ($E_{VBMB}$) of an undefective NiO crystal, where $\mu_e$ was varied from 0 to the calculated bandgap energy of NiO. The last term in (1) represents the energy corrections needed for the charged defects to counter the self-interaction originated from the periodic boundary conditions of finite supercells. The charge states of defects were set by removing or adding electrons from the considered supercell. The Madelung potential of the 64 and 512 atoms NiO supercells was calculated to be 0.0585 and 0.0292 eV, respectively, using the DFT-calculated macroscopic static dielectric constant $\varepsilon = 5.79$, which is close to the experimental value of $\varepsilon = 5.7$ [38]. This small Madelung potential implies that the charge–charge self-interaction is small. Nevertheless, we introduced an image-charge correction to minimize the long-range Coulomb interaction for the charged defects and its periodic image. We utilized the Lany and Zunger correction [39] calculated by noncubic adaptation code, DeFAP, as implemented by Hine and Murphy, which is 0.65 times the Coulomb-only point charge correction schemes to account for potential alignment [40] to the formation energy calculated using the 64 atom supercell.

The chemical potential ($\mu_i$) of Ni, O, and extrinsic metal cations were calculated using the literature method [26], [37]. This method assumes that the transition metal dopants are in thermodynamic equilibrium with a reservoir of TMO when they are synthesized under O-rich conditions, which is the case for most NiO films. Commonly, the chemical potential of the defective species is calculated through DFT simulations of their oxide. However, these metal oxides often require an additional U parameter of a different value from that used to simulate the dopant in NiO, which causes a problem in comparing the formation energy across different phases. Instead, the chemical potential can be written in terms of the Gibbs free energy of formation of the respective binary metal oxide ($M_xO_y$) in the standard growth conditions ($T^0 = 298.15 K$, and $pO_2^0 = 1 atm$), as follows:

$$\Delta G_f^{M_xO_y}(pO_2^0, T^0) + x \mu_{M(s)} - \frac{x}{2} \mu_{O(s)} - \frac{y}{2} \mu_{O_2}$$

(2)

where $\mu_{M(s)}$ is obtained from the DFT calculation of the parent metal crystal (e.g., fcc Ni), and the Gibbs free energy $\Delta G_f^{M_xO_y}(pO_2^0, T^0)$ was taken from the standard free energy tables [41]. Compared with a gaseous phase, the dependence of a solid phase on temperature and partial pressure can be considered negligible. The chemical potential of the constituents $M$ and $O$ must be equal to the chemical potential of $M_xO_y$; therefore, it can be written as follows:

$$\mu_{M_xO_y(s)} = x \mu_{M(M_xO_y)} + y \mu_{O(M_xO_y)}.$$  

(3)

When the $M_xO_y$ is in thermodynamic equilibrium with the environment, then the oxygen chemical potential at a temperature ($T$) and oxygen partial pressure ($pO_2$) can be written as

$$\mu_{O(M_xO_y)}(pO_2, T) = \frac{1}{2} \mu_{O_2(g)}(pO_2, T).$$

(4)

From (3) and (4), the $\mu_{M}$ at $T$ and $pO_2$ can be written as

$$\mu_{M(M_xO_y)}(pO_2, T) = \frac{1}{x} \left( \mu_{M_xO_y(s)} - \frac{y}{2} \mu_{O_2(g)}(pO_2, T) \right).$$

(5)

Combining (2) and (5), the $\mu_{M}$ in $M_xO_y(s)$ can be written as

$$\mu_{M(M_xO_y)}(pO_2, T) = \frac{1}{x} \left( \Delta G_f^{M_xO_y}(pO_2^0, T^0) + x \mu_{M(s)} \right) - \frac{y}{2} \mu_{O_2(g)}(pO_2, T)$$

(6)

where the $\mu_{O_2(g)}$ at a nonstandard condition $T$ and $pO_2$ is obtained from the rigid-dumbbell ideal gas model [26], [42], [43]. This approach ensures the consistency of the $\mu_i$ of constituent elements for subsequent defect formation energy calculations.

B. Synthesis of the Ternary Al$_x$Ni$_y$O by ALD

The Al$_x$Ni$_y$O films were synthesized by ALD onto single-side polished 500 µm thick Czochralski (Cz) Si wafers and double-sided polished 180 µm thick 2.0 Ω cm p-type Cz Si wafers for material characterization and contact resistivity measurements, respectively. The c-Si wafers were cleaned using a standard Radio Corporation of America (RCA) cleaning with or without a final dip in 2% w/v HF solution to either remove or intentionally leave the native SiO$_2$ layer onto c-Si prior to the deposition of Al$_x$Ni$_y$O films. The ultrathin native SiO$_2$ resulting from the RCA process acts as a nucleation site for the initial growth of the TMOs. The Al$_x$Ni$_y$O was deposited using the ALD super-cycle approach considering the growth rate per cycle (GPC) of the constituent-involved oxides [24], [25]. For example, to deposit the Al$_x$Ni$_y$O, bis-(N,N'-di-t-butylacetamidinato) nickel (II), trimethylaluminum (TMA), and H$_2$O were used as precursors for Ni, Al, and O, respectively, at a deposition temperature of 150 °C. Based on the GPC of NiO and Al$_2$O$_3$, the ALD super-cycles were varied to obtain different Al content into the ternary NiO. An Al$_2$O$_3$ to NiO cycle ratios of 1:50 was used to obtain an Al$_x$Ni$_y$O film with a relatively low Al concentration.

The deposited films were characterized by spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and contact resistance measurements. The XPS measurements were conducted using Escalab 250Xi, and spectra were analyzed using the Avantage software. The hole selectivity was evaluated by using the Cox and Strack method, where Pt/Ag bilayer was deposited by e-beam and thermal evaporation, respectively. The thermal stability of the
**Fig. 1.** Magnetic ordering of a pristine NiO $2 \times 2 \times 2$ supercell with (a) AFM-I and (b) AFM-II configurations. The translucent blue and green planes represent planes of atoms with the same spin along the (100) and (111) planes for AFM-I and AFM-II.

contact was measured by annealing the samples in a rapid thermal process system (RTP-600xp) in a 5000 sccm $N_2$ atmosphere for 10 min at different temperatures of 180—400 °C.

### III. RESULTS AND DISCUSSION

#### A. Structural Properties of Pure NiO

Localized d-electrons of transition metal cations result in a large local magnetic moment and magnetic ordering. At room temperature, NiO has the sodium chloride (NaCl)-type crystal structure with the space group of $Fm\bar{3}m$ where atoms are arranged in octahedral coordination and exhibits spin polarization with AFM ordering on the Ni sublattice, up to the Néel temperature of 523 K [44]. Two AFM structures, called AFM-I and AFM-II, following the nomenclature of previous studies [45] were considered (see Fig. 1). Magnetic moments in the AFM-II structure were alternated across neighboring (111) planes. Of the two structures considered, the AFM-II resulted in the lowest energy in the DFT calculations, in agreement with the literature [34] and [46]. Therefore, all further calculations were conducted considering the AFM-II NiO magnetic structure. A slight distortion of the cubic crystal lattice was also observed due to the AFM arrangement of the spin on the Ni atoms, leading to a rhombohedral lattice. This distortion is also consistent with the published literature [46].

The GGA+U calculated lattice parameters, Ni-O bond lengths, local magnetic moments, and bandgap energies of NiO are listed in Table III. The relaxed lattice parameter for the bulk AFM-II NiO structure was found to be 4.18 Å, which matched well with an experimental lattice of 4.17 Å [31] and with previous DFT studies. The calculated Ni-O bond length of 2.09 Å and local magnetic moment on Ni atom of 1.69 μB for the pristine NiO are also in good agreement with experimental DFT literature [47]. The calculated bandgap of 3.2 eV for the pristine NiO is smaller than its experimental counterpart of 3.6–4.3 eV, which is not unexpected as semi-local DFT often underestimates the bandgap of metal oxides [48], and is corrected when a hybrid functional is used instead (4.6 eV, from our HSE06 calculations). As shown in Table III, the structural properties of NiO from GGA+U calculations with an appropriate U parameter were comparable to data obtained from the HSE06 hybrid calculations.

#### B. Intrinsic Defects Properties of Pure NiO

The electronic DOS of a pristine 64 atoms NiO supercell, presented in Fig. 2(a), shows that the VB predominantly consisted of O 2p and Ni 3d states and reflected the covalent bonding nature originated from significant hybridization between the Ni 3d and O 2p orbitals. However, as shown in Fig. 2(b), the O 2p contribution dominated the VBM, confirming its charge transfer and Mott-Hubbard type characteristics. A wide VB of 6.9 eV was observed, as well as a CB dominated by the Ni 3d states, both of which agree with the literature [33] and [34]. As the $p$-type characteristics of NiO are resulting from its non-stoichiometry, the DFT calculations were first focused on intrinsic $V_{Ni}$ and $V_{O}$ defects to reveal the electronic properties of NiO. Interstitial defects of Ni and O are unlikely to form spontaneously because of the high defect formation energies originated from the densely packed NaCl-type structure [35]. The band structure also reveals the indirect bandgap [51], where the bandgap was determined by the highest VB states and the lowest CB states resulting from O 2p states and Ni 3d states, respectively.

### Table III

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<th>Ni-O bond length (Å)</th>
<th>Ni magnetic moment (μB)</th>
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Fig. 2. Calculated (GGA+U) electronic structure of pristine NiO. (a) Spin-polarised total and species-projected DOS where the dashed vertical line indicates the Fermi energy. (b) Corresponding band structure.

The transition level diagram (see Fig. 3) shows the formation energies of intrinsic defects as a function of Fermi energy within the bandgap of NiO at O-rich growth condition. The oxygen chemical potential was -2.58 eV (i.e., standard conditions of 298.15 K and $p_{O_2} = 0.2$ atm). The lowest energy charge states at the Fermi level are labeled, and filled circles indicate the transition levels.

As shown in Fig. 3, $V_{\text{Ni}}$ was the predominant intrinsic defect under O-rich conditions. At Fermi levels above 1 eV, $V_{\text{Ni}}$ was fully charged $V'_{\text{Ni}}$ [53]–[55]. However, the neutral ($V''_{\text{Ni}}$) and $+1$ charge states $V''_{\text{Ni}}$ were stable up to 0.32 and 1.05 eV with respect to the VBM, respectively (see Fig. 3). The slightly lower $V''_{\text{Ni}}$ formation energies of 0.32 eV compared with previously reported (0.48 eV) [48] were believed to arise from the size of supercell and choice of using Gibbs free energy at standard conditions to calculate the chemical potential of constituent elements nickel and oxygen. The negative energies for $V'_{\text{Ni}}$ and $V''_{\text{Ni}}$ defect formation indicate that these native defects are easier to form compared with the charge-neutral $V_{\times\text{Ni}}$ in identical growth conditions. The formation energies are particularly sensitive to the DFT description of $O_2$ gas molecules, sometimes used to define the chemical potential for O. Therefore, we used the standard Gibbs free energies of formation of NiO to calculate chemical potential and consequently the formation energy of the defect species in NiO. This reduces the sensitivity of the results on the DFT simulation parameters [26], [42].

As the growth of materials depends on the deposition conditions, the intrinsic defects, $V_{\text{O}}$ [see Fig. 4(a)] and $V_{\text{Ni}}$ [see Fig. 4(b)], were first considered. The DOS of pure NiO shows no defect states within the bandgap [see Fig. 2(a)]. However, the intrinsic $V_{\text{O}}$ and $V_{\text{Ni}}$ induce defect states within the NiO bandgap, and their position changes with defect charge. The $V_{\times\text{O}}$ in NiO leads to the formation of two defect levels which is resulted from the structural geometry optimization: a filled defect state at 1 eV above the VBM and another empty defect level 0.3 eV below the conduction band minimum (CBM), indicating a donor-type electronic structure. The electrons around $V_{\times\text{O}}$ can be excited to the CB.

The dominating defect states close to the CB originate from the Ni 3d orbital, and the one close to the VBM is contributed mainly by O-2p orbital contribution. These impurity states result from dangling bonds of Ni, which are a coordinating oxygen vacancy site. A singularly charged oxygen vacancy, $V_{\bullet\text{O}}$, appeared spin-polarized with the splitting of both defect states. Only the lowest state occupied and empty deep defect bands at
Fig. 4. Calculated spin-polarized total and species-projected DOS plots of NiO containing (a) an oxygen vacancy and (b) a nickel vacancy. The Fermi level was set to zero.

0.8 eV above Fermi level in spin-up states are deep trap states. In contrast, two shallow defects with spin-up and spin-down states were observed close to the CB edge. The empty defect bands for the $V_{O}^{\text{\cdot\cdot}}$ defects were close to the CBM. However, as suggested by the formation energy (see Fig. 3) it was unstable at a high Fermi level under the O-rich condition.

For typical growth conditions, NiO shows $p$-type conductivity due to the presence of $V_{\text{Ni}}$, which is the predominant and most stable defect under the O-rich conditions. As shown in Fig. 4(b), the empty states created by the $V_{\text{Ni}}$ were shallow and closer to the VB of c-Si, thereby participating in hole conduction through these shallow states of NiO. It is understood that the $V_{\text{Ni}}$ defects create dangling oxygen bonds, which result in localized defect states. These trap states were within a shallow defect level, approximately 0.3 eV above the VBM of NiO, in close agreement with the experiments by Flynn et al. [56], [57] which showed that these defects were associated with $V_{\text{Ni}}$ are located at 0.4 eV above the VBM. Oxygen atoms around $V_{O}^{\text{\cdot\cdot}}$ and nickel atoms around $V_{\text{Ni}}^{\text{\cdot\cdot}}$ in their relaxed NiO structure were found to move outward by 8% and inward by 3%, respectively.

C. Doping of NiO With Metals

The electrical conductivity of TMOs can vary from insulating to semiconducting to metallic based on their doping asymmetry characteristics and capability to accommodate various types of defects. Most TMOs suffer from insufficient electrical conductivity for application in solar cells and electrocatalysis. Incorporating multivalent transition metal cations could be a viable approach to transforming NiO from insulating to semi-metallic upon partially filling the $d$-orbital and change of cation oxidation states. The changeable oxidation states of metal dopants could result in favorable gap states within NiO, creating pathways for charge transport, thus enhancing the electrical conductivity of NiO. Knowing the solubility limit of these metal cations in NiO is important for obtaining a single-phase material with enhanced charge-carrier dynamics.

As this study focuses on typical substitutional extrinsic defects of commonly used ALD metal precursors, the following dopants were considered, and their effect on the electronic properties of NiO was predicted using DFT calculations: W, Ta, Nb, Mo, Si, Sn, Ti, Zn, Al, Mg, and Hf. Equation (6) was used to calculate the chemical potential of these dopants where Gibbs free energy at standard condition was used for the respective stable metal oxides $\text{WO}_3$, $\text{Ta}_2\text{O}_5$, $\text{Nb}_2\text{O}_5$, $\text{MoO}_3$, $\text{SiO}_2$, $\text{SnO}_2$, $\text{TiO}_2$, $\text{SrO}_2$, $\text{ZnO}$, $\text{Al}_2\text{O}_3$, $\text{MgO}$, and $\text{HfO}_2$ [41]. The transition level diagram (see Fig. 5) shows formation energies of extrinsic defects at the most favorable charge states at standard conditions of 298.15 K and $p\text{O}_2 = 0.2$ atm.

The synthesis and subsequent post-deposition temperature and $p\text{O}_2$ significantly impact the stability of the final structure of ternary NiO. Controlling the defects’ chemistry and charge states...
of materials is crucial because it leads to potential applications. For instance, increasing conductivity by introducing shallow defect states is required for solar cells and enhancing surface defects required for potential electrocatalyst applications. As shown in Fig. 5, the investigated extrinsic defects are predicted to be often accommodated as charged defects. For example, the charge-neutral state of Ta$_{Ni}$ defect possesses a higher defect formation energy and is only stable at a higher Fermi level compared with the charged defects of Ta$_{Ni}^{\ddagger}$, Ta$_{Ni}^{-}$, and Ta$_{Ni}^{3+}$ (equivalent to Ta cations in 5+, 4+, and 3+ oxidation states, respectively, on the Ni$^{2+}$ lattice site).

The total spin-up DOS of the pristine NiO is also shown for comparison. The GGA+U calculations show that while most of the dilute dopants introduce bandgap defect states (i.e., Ta$_{Ni}^{\ddagger}$, Zn$_{Ni}^{\ddagger}$, Al$_{Ni}^{\ddagger}$, Mg$_{Ni}^{\ddagger}$, Hf$_{Ni}^{\ddagger}$, Ti$_{Ni}^{\ddagger}$, W$_{Ni}^{\ddagger}$, Nb$_{Ni}^{\ddagger}$, Mo$_{Ni}^{\ddagger}$, Sr$_{Ni}^{\ddagger}$, Si$_{Ni}^{\ddagger}$, and Sn$_{Ni}^{\ddagger}$), some of the substitution defects in their fully charged valence state (i.e., Zn$_{Ni}^{-}$, Al$_{Ni}^{-}$, Hf$_{Ni}^{-}$, Sr$_{Ni}^{-}$, and Sn$_{Ni}^{-}$) do not create defect states in the bandgap. These dopant defects in their lower charge states, however, show multiple defect energy levels (i.e., Nb$_{Ni}^{-}$, W$_{Ni}^{-}$, Ta$_{Ni}^{-}$, Mo$_{Ni}^{-}$, Al$_{Ni}^{-}$, Sr$_{Ni}^{-}$, Hf$_{Ni}^{-}$), confirming that some of these defects could play some roles in charge carrier’s transport pathways, provided that they are stable at relatively low Fermi energies. Some dopants, including W, Mo, and Ta, exhibit positive formation energy at all Fermi levels, implying that these are difficult to incorporate into NiO. On the other hand, a few defects, such as Al, Sr, Nb, Si, Sn, Ti, and Zn, exhibit negative formation energy when the Fermi level is close to the VBM, indicating a high solubility at Fermi level. Singly charged Sr$_{Ni}^{\ddagger}$ is more easily accommodated at a low Fermi level, but the neutral charge state dominates most electron energies in the NiO bandgap. The bandgap energy also reduces with some elemental doping; for example, Sr doping causes a decrease of NiO bandgap, consistent with published data in the literature [58]. Al$_{Ni}^{\ddagger}$ is the more easily accommodated compared with Al$_{Ni}^{\ddagger}$ for most of the Fermi energy range. Defects, such as W$_{Ni}^{-}$, Ta$_{Ni}^{-}$, and Mo$_{Ni}^{-}$ exhibit unfavorable formation energies compared with other defects, such as Si$_{Ni}^{\ddagger}$, where $q$ denotes the Fermi level-dependent charge states. While the +4 and +3 charge states were expected for Mo$_{Ni}^{q}$, it appears that Mo$_{Ni}^{2+}$ only adopts a +2 and +1 charge state.

### D. Hybrid DFT Calculations for Doped NiO

At first, the GGA+U method was used to address the spurious self-correlation of d and f electrons of transition metals, resulting in incorrect DOS values. However, some delocalization could still occur because of the lack of universality of the GGA+U method [59]. In addition, a higher U value could lead to the deterioration of other material properties. The use of hybrid functionals prevents delocalization and produces more accurate electronic bandgap and electronic states because they enable orbital-dependent nonlocal exchange-correlation potential. However, it is impractical to perform geometry relaxations for large supercells. Because of computationally expensive hybrid calculations, the scaled hybrid method [26] was used to calculate DOS for the most promising defect states instead of a full atomic relaxation using HSE06.

As shown in Fig. 6, the HSE06 calculated defect formation energies were different from those obtained with the GGA+U approach, presented in Fig. 5. The obvious difference is the energy gap which is larger for the hybrid calculated NiO. While a large U value applied to Ni in the GGA+U could result in bandgap defects close to the experiments, Ni magnetic moment, and structural properties could be compromised when a very large unphysical U parameter is used. In addition, determining the relative energetic positions of dopant states compared with the host lattice is problematic in the GGA+U approach. For example, as shown in Fig. 5, while Al$_{Ni}^{\ddagger}$ is stable up to 2.8 eV within the GGA+U calculated bandgap energy of 3.2 eV, it is stable up to the Fermi energy of 3.8 eV within the hybrid DFT calculated bandgap energy of 4.6 eV (see Fig. 7). Subsequently, a change in formation energies of dopants at their various charge states was observed between the GGA+U and hybrid DFT approaches. As the hybrid approach results in more accurate bandgap and positions of dopant states, the hybrid approach was also used to compare the dopants study with the GGA+U approach. The thermodynamic transition level diagram shows that the formation energies for Mg and Zn were low across the wide range of Fermi energies in their charge-neutral states. The Ti$_{Ni}^{\ddagger}$ is dominant up to the Fermi energy of 2.4 eV while the Ti$_{Ni}^{-}$ is close to the CB, suggesting that the latter is a donor defect. It also shows that W and Sn cannot be incorporated into NiO because of high defect formation energies.

The total DOS calculated using the hybrid method showed that defect states created by Mo$_{Ni}^{q}$ at 0.4, 1.2, and 1.5 eV for +2, +1 and neutral charge states, respectively, were closer to the VBM [see Fig. 7(a)] compared with that of the GGA+U with values of 1.4, 2.0, and 2.2 eV, confirming the qualitative difference between the formation energies for the two approaches. As shown in Fig. 7, doping of NiO leads to the formation of several states in NiO bandgap, where dopant-derived states often show a difference in the spin up and spin down, which results in a magnetic moment. A smaller Al-O bond length of 1.84 Å was observed for Al$_{Ni}^{3+}$ compared with the Ni-O bond length of
The HSE06 results show that the charge-neutral $\text{Al}_{\text{Ni}}^{+}$ dopant leads to the formation of several states in the bandgap (close to VB and in mid bandgap), both in agreement with the GGA+U calculations. The $\text{Al}_{\text{Ni}}^{+}$ results in defect states in the bandgap of NiO created by 2+ oxidation state of Al, which likely to occur only at high Fermi levels. These dopant-derived DOS show a small excess of spin-up over spin-down states and form the highest occupied states, lying below the Fermi level of the $\text{Al}_{\text{Ni}}\text{Ni}_3\text{O}$. These mid-gap states of $\text{Al}_{\text{Ni}}^{+}$ act as Shockley-Read-Hall carrier recombination centers to trap photogenerated charge carriers and are not expected in solar cell applications. The reduction of NiO bandgap upon Al doping could arise from unoccupied dopant-induced states above the highest occupied state, resulting in a narrow bandgap for the $\text{Al}_{\text{Ni}}\text{Ni}_3\text{O}$. The unoccupied Ni 3d state at the bottom of the CB for the $\text{Al}_{\text{Ni}}$ suggests that Ni contributes to the gap states. However, $\text{Al}_{\text{Ni}}$ is stable as a positively charged $\text{Al}_{\text{Ni}}^{2+}$ for most of the Fermi levels up to 2.8 eV and results in defect levels close to the band edge. In this regime, the defect states close to the CBM of NiO are expected to work as a shallow donor defect because of the free electron released to CB resulting from the replacement of Ni$^{2+}$ by Al$^{3+}$. At higher concentrations, the defect–defect interactions might create deep-level defect states within the bandgap. This is not investigated here as the simulations represent dilute defects with an effective concentration of 3.12 at% dopants. The defects such as Hf, Ti, Mo, Si are expected to act as donor defects at high Fermi energies, but the multivalent dopants, such as Al, Si, Ti, Mo, Nb, and Hf create defect states close to the NiO VB, are expected to act as a photogenerated charge carrier transport pathway from c-Si to the contact in a c-Si solar cell; thus, improving its charge collection efficiency.

### E. Experimental Synthesis of $\text{Al}_{x}\text{Ni}_y\text{O}$ by ALD

As shown in Figs. 5 and 6, the DFT analyses show that $\text{Al}_{x}^{+}$ is more stable than $\text{Al}_{x}^{2+}$ up to a Fermi energy of 2.7 eV for GGA+U and 3.8 eV for hybrid calculations. Fig 7 shows that the defect states introduced by $\text{Al}_{\text{Ni}}^{+}$ are close to the band edges. Therefore, these defect states of $\text{Al}_{x}\text{Ni}_y\text{O}$ could act as transport pathways of the photogenerated charge carrier from c-Si to the metal contact, suggesting potential conductivity improvements for the $\text{Al}_{x}\text{Ni}_y\text{O}$ films. Therefore, approximately 8.5 nm thick $\text{Al}_{x}\text{Ni}_y\text{O}$ film was synthesized by ALD. The electronic structure and chemical composition of the $\text{Al}_{x}\text{Ni}_y\text{O}$ film deposited onto c-Si/SiO$_2$ substrate and the interface composition in c-Si/SiO$_2$/Al$_x$Ni$_y$O stack layers were analyzed by XPS surface and depth profiling measurements, respectively. The concentration of Al in the $\text{Al}_{x}\text{Ni}_y$O film was estimated to be higher than the $\text{Al}_2\text{O}_3$:NiO ALD supercycles ratios of 1:50 (Al:Ni), resulting from much higher growth per cycle of the $\text{Al}_2\text{O}_3$ than NiO during growth by ALD (see Table IV) [60].

The XPS revealed the stoichiometry of the film was $\text{Al}_{0.21}\text{Ni}_{0.75}\text{O}$ resulting from the significantly lower growth per cycle of NiO versus $\text{Al}_2\text{O}_3$ and some nucleation delay for the deposition of ALD NiO. This was also reported by Baker et al. [60], a significantly higher uptake of Al than Ni toward the formation of $\text{Al}_{0.21}\text{Ni}_{0.75}\text{O}$ from their binary $\text{Al}_2\text{O}_3$ and NiO ALD cycles, confirming a nickel deficient (Al-rich) $\text{Al}_{0.21}\text{Ni}_{0.75}\text{O}$ film.
The deconvoluted O 1s spectra show a peak binding energy (BE) of 529.9 eV corresponding to the presence of Ni[^2+](NiO), and the peak BE around 531.1 eV confirms lattice oxygen associated with the Ni-O and Al-O bonds [Ni[^3+], AlO[^3-], and AlO(OH)]. The peak intensity increased in Al_{0.21}Ni_{0.75}O films, which can also be attributed to Al-Ni bonding, suggesting that the Al_{0.21}Ni_{0.75}O film was more oxidized than pure NiO. The peak BE of 74.0 eV for Al 2p$_{1/2}$ and the absence of the peak at 71.9 eV for metallic Al 2p further confirm the incorporation of Al[^3+] into NiO [21]. The UPS analyses [see Fig. 8(b)] show a shift in the VB of NiO with respect to the Fermi level, which could be explained by the incorporation of Ni[^3+] states in the NiO film. The work functions of the pure NiO, and Al_{0.21}Ni_{0.75}O films were measured to be 4.51, and 4.68, respectively, suggesting an increase of p-type characteristics upon Al incorporation. The work function of NiO typically ranges from 4.4–5.6 eV, depending on their surface composition and crystalline orientation [62].

The ToF-SIMS profiles show constituent elements Ni, O, and Al in the c-Si/SiO$_2$/Al$_{0.21}$Ni$_{0.75}$O stack layers and their variation with sputter time [see Fig. 9(a)], which was further verified by the XPS depth profiling measurements [see Fig. 9(b)]. It demonstrates a homogeneous distribution of constituent elements across the film thickness. The increase of Si intensity with sputter/etch time reveals a 1 nm thin SiO$_2$ layer, originated from the RCA process prior to ALD. The ToF-SIMS profiles indicate the presence of hydrogen resulting from incomplete combustion of the ALD precursors.

### F. Contact Performance of the Al$_{0.21}$Ni$_{0.75}$O Films With C-Si

As shown in Fig. 10(a), the undoped NiO does not provide an ohmic contact on c-Si. A contact resistivity ($\rho_{c}$) with a minimum value of $\sim$331 m$\Omega$ cm$^2$ was obtained for the as-deposited Al$_{0.21}$Ni$_{0.75}$O film [see Fig. 10(a)]. This significantly reduced contact resistivity compared with undoped NiO is likely caused by the energy level of the shallow defects of Al$_{0.21}^+$ within the bandgap, as suggested by the DOS. Pure NiO tends to crystallize at the ALD growth temperature of 150 °C, often detrimental to the passivating contact performance. Therefore, the films were subsequently annealed at 180–400 °C using the rapid thermal annealing process in N$_2$ for 10 min. The Al$_{0.21}$Ni$_{0.75}$O film was found to be thermally stable up to 300 °C, and the film showed a minimum contact resistivity $\rho_{c}$ value of 470 m$\Omega$ cm$^2$ [see Fig. 10(b)]. A rapid increase of the carrier concentration and a decrease of NiO resistivity were previously reported by a higher concentration of Al[^3+] dopants, which releases an electron in the CB of NiO [63]. In addition, the incorporation of Al reduces the crystallinity of the Al$_{0.21}$Ni$_{0.75}$O films [64]. These results suggest that the addition of Al in NiO keeps the film amorphous at
higher annealing temperatures, which is desirable for a low contact resistivity. We previously demonstrated contact resistivity values of 59.3 and 21.5 mΩ cm² for c-Si/Zn₀.₆₂Ni₀.₃₈O in the as-deposited state and after annealing at 200 °C, respectively, and the films were thermally stable up to 500 °C [22].

The effect of Al incorporation into NiO and consequent change of composition and contact performance of the films can be attributed to the deficiency of Ni in the top layer of the as-grown films as shown by XPS depth profiles [see Fig. 9(b)]. In metal oxides, both anion and cation deficiency increase conductivity, and the latter case has been observed for the as-deposited samples. Here, the contact performance of the c-Si/SiO₂/Al₀.₂₁Ni₀.₇₅O stack improved because of an increased conductivity of the Al₀.₂₁Ni₀.₇₅O films. This shows that the improved contact performance of the doped NiO originated from higher conductivity as an interfacial layer with enhanced electrical conductivity plays a crucial role in obtaining improved contact performance. The crystallization step during the post-processing could be responsible for the reduced contact resistivity of the Al-containing films. These results agree well with the enhanced contact performance, as shown in Fig. 10. After annealing at temperatures higher than 300 °C, however, the films were unstable, which could result from the crystallization of the deposited films or the release of hydrogen, affecting the contact performance of the deposited materials.

**IV. CONCLUSION**

In this article, we first systematically investigated the effects of intrinsic and extrinsic defects in NiO by DFT calculations and demonstrated how they result in defect states within the bandgap and close to the VB of NiO. We used standard and hybrid DFT approaches to investigate and obtain suitable dopants for NiO. It was shown that intrinsic nickel vacancy defects are predominant and result in p-type conductivity; however, their density is insufficiently high for an effective hole-contact with p-type c-Si. Guided by the DFT calculations, AlₓNi₀.₇₅O films were deposited by ALD and used as hole-selective contact with c-Si. The obtained minimum contact resistivity values of 331 and
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