



Preparation of semi-transparent V_2AlC thin films using the thermionic vacuum arc technique: crystal and substrate effects on the electrochemical performance

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Abstract Among the MAX phases, vanadium aluminum carbide (V_2AlC) is one of the remarkable elements due to its superior properties. These intriguing properties stem from physical characteristics such as crystallinity, grain size, and so on, which further affect its electrochemical performance. One of the major and significant issues in this way is using an appropriate substrate to form the desired crystal orientation. According to the results, the crystal nature of the substrate and conductive layer illuminates the formation of polycrystalline V_2AlC with various preferential orientations. This subject also directly changed the electrochemical performance, Li-ion diffusion, and resistivity of the V_2AlC thin film. The XRD, high-resolution XPS, and Raman spectroscopy results revealed V_2AlC formation on all substrates. In all cases, the surface characteristics were confirmed nano-dimensional growth, with a high level of compactness, homogeneity, and a crack-free landscape. Moreover, the optical measurements exhibited semi-transparency of the thin film with lower disorder but higher cutoff energy when coated upon the ITO/PET substrate. The electrochemical results highlighted that the V_2AlC coated upon the ITO/PET platform outperforms due to non-Faradaic behavior, lower disorder, and small grain size, facilitating Li-ion diffusion and more capacity storage behavior inside the aqueous $LiClO_4$ -PC (0.1 M). Subsequently, the selected material paved the way for using it as a promising candidate in metal-ion storage.

1 Introduction

Various researchers and industries are in great demand for emerging materials with superior properties. Among the latest types of materials, the MAX series has globally attracted scientists. All MAX phases are stacked layers of hexagonal structures with the symmetry space group $P6_3/mmc$, each containing two formula units. In the MAX phase, octahedral sites are filled by group ‘X’ atoms, whereas sheets made of the group ‘A’ elements are joined with multilayer sheets in a densely packed structure [1]. The M-A bond in the MAX phase is metallic, whereas the M-X bond consists of ionic, metallic, and covalent bonds. Because of the tight connection between the layers, these MAX phases are more challenging to exfoliate mechanically than graphene or other 2D materials. The M-A bond is significantly weaker than the M-X bond. The ‘A’ layer of the MAX phase can be deliberately removed by introducing an acidic or molten salt solution, but this will not impact the M-X bond [2]. Removing ‘A’ sheets from their MAX phases is known as ‘MXenes.’

MAX phase alloys are a group of alloys that began to be used in high-temperature applications in the late 1960s. Due to their crystal structure properties, they are also defined as layered alloys. ‘M’ denotes an early transition metal such as (Mo, Mn, Cr, Zr, Ti, Ta, Nb), and ‘A’ can refer to 13 or 14 group elements, such as (Si, Sn, Al, Sb, Cd, P). ‘X’ can refer to either carbon or nitrogen. The variable’s value denoted by ‘n’ can be represented by any of three distinct integers: $n=1-4$ [3]. Although there are more than a hundred MAX phase structures, the types commonly encountered in industrial applications appear with three separate hexagonal crystal lattice systems: the ‘211’ MAX phases, such as (Ti_2AlC , V_2AlC , Ti_2AlN), ‘312’ MAX phases, such as (Ti_3AlC_2 , V_3AlC_2 , Ti_3SnC_2), and ‘413’ MAX phases, such as (Ti_4AlN_3 , V_4AlC_3 , Ti_4SiC_3) [4]. These lattice structures are given in Fig. 1.

The difference between the three structures depends on how many M layers separate the A layer. MAX phase alloys combine the superior properties of ceramic and metallic phases, and these materials are also defined as transition materials between metallic and ceramic materials. They have light and robust structures, good thermal and electrical conductivities, good thermal shock resistance, good machinability, high-temperature oxidation resistance, good thermal shock resistance, high-temperature durability, low thermal expansion coefficients, and good wear and corrosion resistance [5–7]. MAX phases can be used in aerospace industries

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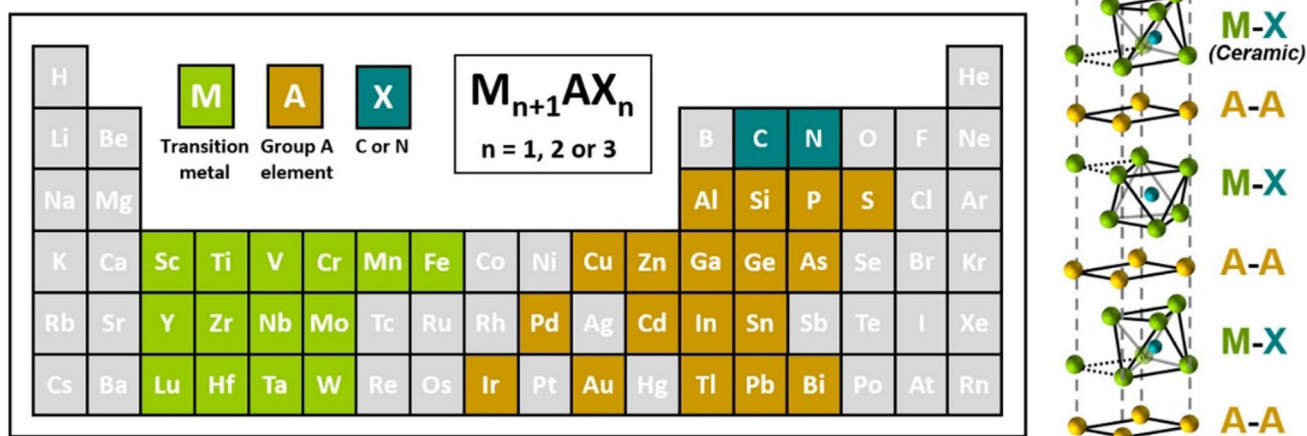


Fig. 1 The elements used in the MAX family and the crystal structure of the family

as high-temperature heating elements, electric–electronic industries as coatings for electrical contacts, and battery industries as supercapacitors.

Several techniques have been employed to create MAX phases, including hot isostatic press [8], high-temperature synthesis [9], self-propagating high-temperature synthesis [10], and spark plasma sintering/pulse discharge method [11]. Hot pressing is a standard method for creating dense MAX phase samples with high phase purity. In this method, a graphite die is filled with the powder, which is then uniaxially compressed between two graphite punches and heat-treated under argon or vacuum. During the process, the temperature ranges between 1000 and 1700 °C, while the pressure is up to 50 MPa [12].

The hot isostatic press is similar to the hot press, which leads to pure and dense MAX phases [13]. Because of the isostatic press, there is no preferential grain orientation or texturing in the MAX phase. However, this method is less used than hot pressing. In self-propagating high-temperature synthesis, MAX phases are formed due to the ignition of powder mixtures under vacuum in the exothermic reactions. As a result, a large quantity of MAX powders is developed. This method seems to be one of the best techniques for producing MAX powders [14, 15]. Pressureless synthesis is straightforward to apply to obtain the MAX phases. The pellets are placed in the crucible heated for a few hours to about 1400 °C in an argon environment or vacuum. Therefore, some carbides or nitrides are found at higher temperatures due to the deterioration of MAX phases [16]. Sample preparation in spark plasma sintering is similar to hot pressing but has different thermal cycles. Compared to hot pressing, spark plasma sintering allows for faster heating rates, lower temperatures, and shorter dwell times [17].

Among these large families, V_2AlC is explored by different groups. Compared with other MAX series, there are a few number of research and published papers in the literature based on V_2AlC . Significantly, using the material as thin film is restricted to recent publications. To surpass this challenge, we are concentrating on V_2AlC material as a thin film on conductive layers such as indium tin oxide (ITO) and fluorine-doped tin oxide (FTO). Importantly, to understand the effect of substrate on V_2AlC thin film, two different substrates, i.e., glass and polyethylene terephthalate (PET), were selected.

This study examined coatings produced by the TVA method from V_2AlC pellets. The effects of structure, such as crystallinity and film quality, surface morphology, optical characteristics, and electrochemical performance, on the V_2AlC films were briefly evaluated. X-ray diffraction (XRD), X-ray photoelectron spectrometer (XPS), field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), ultraviolet–visible spectroscopy (UV–VIS), and electrochemical analyses of the coated V_2AlC thin films on three different substrates were used for this purpose. All of the coated thin films exhibited a crystalline structure.

2 Material and Method

2.1 Experimental detail

The V_2AlC MAX micron powder (99 + % purity) was purchased from the Nanografi company (Turkey). Also, the ITO/glass, FTO/glass, and ITO/PET were purchased from the Teknoma company (Turkey). V_2AlC MAX powder was produced as a pellet at 10 bar pressure. The pellet diameter and thickness were 1 and 1 mm, respectively. ITO/glass, FTO/glass, and ITO/PET were used for substrates, and these substrates were ultrasonically cleaned with deionized water (50 °C) for 5 min to remove the particles on the substrates.

Table 1 The effective parameters during the coating of V_2AIC through the TVA technique

Parameters	$V_2AIC/ITO/glass$ $V_2AIC/FTO/glass$ $V_2AIC/ITO/PET$
Discharge current (A)	0.2
Deposition time (s)	60
Working pressure (Torr)	3×10^{-4}
Applied voltage (V)	800 $\rightarrow$ 300
Filament current (A)	19

The Thermionic Vacuum Arc (TVA) technique is a physical vapor deposition (PVD) method for producing thin films. Unlike other PVD methods, the TVA technique is versatile compared to other plasma-assisted techniques. It can coat glass, polyethylene (PET), silicon (Si), ceramic, metal, and other substrates. Besides, the TVA technique is remarkably rapid for coating films.

The method is based on creating a plasma of anode material in a high vacuum. No buffer gas is used during this process, and the discharge is the plasma of pure anode material without any gas mixture. The TVA method is a thin-film production method that can produce plasma of almost any material with low or high melting temperatures. There are many publications in the literature on the technique. In the route, the material placed in the anode electrode can be metal, ceramic, or semiconductor and is bombarded with electrons generated by the cathode electrode. The anode electrode used here is a spoon-shaped tungsten or molybdenum crucible. The cathode electrode is a 500- μm -diameter tungsten filament with 4 or 5 turns. The distance between the anode and cathode electrodes is approximately 3–4 mm. The electrons emitted from the cathode focus on the anode material through a Wehnelt cylinder. Current is passed through the tungsten filament utilizing a low-voltage power supply. This causes the tungsten filament to heat up and produce thermionic emission. At the same time, a high voltage is applied between the electrodes. This voltage accelerates the electrons and heats the material in the tungsten or molybdenum crucible. The thermionic energy transferred by the electrons to the anode causes the material in the anode to first melt and then evaporate continuously (Table 1). If the voltage between the electrodes is increased, a bright discharge of anode material vapor is formed in the inter-electrode space at a suitable voltage value. This discharge is a pure material vapor discharge. As a result, the desired anode material can be coated as thin films on various substrates [18].

2.2 Characterization methods

The topological distribution after deposition was demonstrated through atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). All measurements with AFM (Ambios Q-Scope) occurred at room temperature and inside a vibration-isolated chamber with dimensions in the $5 \times 5 \mu\text{m}$ range. Surface morphologies of the V_2AIC films were analyzed by AFM (Ambios Q-scope Atomic Force Microscope) device in non-contact mode using the Scan Atomic V 5.1.0 SPM control software at room temperature. The NSC 16 cantilever was used to examine surface morphologies.

The morphology analysis of the V_2AIC films was characterized with a field emission scanning electron microscope (FESEM) (Hitachi Regulus 8230 model). V_2AIC films were applied gold/palladium alloy deposition a few nanometer layers to improve the surface conductivity in a vacuum environment. FESEM images of films were magnified at 25,000.

X-ray diffraction (XRD) revealed the crystal nature, diverse defect values, and compactness of the layers to analyze the samples' microstructure. This technique also identified the preferred orientation of the V_2AIC .

The V_2AIC film surface chemistry was examined using X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha). The photoelectron peak energies of the V_2AIC film ranged from 40 to 1240 eV.

The optical characterization of the layer was recorded via UV–Vis spectrophotometry and Filmetrics F20. Significantly, the coated layer's transmittance, absorbance, and refractive index behavior are measured at room temperature. To do so, the UNICO dual beam and Filmetrics F20 instruments were implemented.

The electrochemical performance of the samples, such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), was carried out employing a GAMRY Instrument Reference 3000 Device. All measurements were taken using a three-electrode configuration. In this configuration, working, counter, and reference electrodes were selected as produced V_2AIC upon the conductive thin films, Pt wire, and Ag/AgCl, respectively. As a lithium source, $\text{LiClO}_4\text{-PC}$ is used as a liquid electrolyte to evaluate the prepared samples' Li-ion intercalation/de-intercalation performance.

As described in the next section, Raman spectroscopy was used to identify crystals. Renishaw inVia Raman Microscope recorded Raman spectra in the range of $100\text{--}3700 \text{ cm}^{-1}$ using a 532-nm laser source.

FTIR spectroscopy is helpful in analyzing chemical bonds and identifying functional groups in samples. A PerkinElmer Spectrum Two Spectrophotometer was used to obtain the FTIR measurements. The FTIR spectrum ranged from 400 to 4000 cm^{-1} .

Table 2 The surface measurement results obtained by the AFM

	RMS roughness (Sq) (nm)	Skewness (Ssk) –	Kurtosis (Skr) –	Peak valley (St) (nm)	Figure
V ₂ AIC/ITO/glass	2.58	– 0.08	– 0.21	20	a,b
V ₂ AIC/FTO/glass	43.59	0.21	0.46	274	d,e
V ₂ AIC/ITO/PET	14.21	0.58	0.23	86	g,h

3 Results and discussion

3.1 Surface properties

Surface morphology is a critical factor for the device's performance. In this study, FESEM and AFM images were taken to examine the surface properties of V₂AIC films. The AFM and FESEM micrographs of the V₂AIC-coated surfaces are given in Fig. 2. The coated surfaces' microstructure was analyzed by a device with a field emission scanning electron microscope (FESEM, Hitachi Regulus 8230 model). V₂AIC-coated surfaces were applied with gold/palladium alloy deposition in a few nanometer layers to improve the surface conductivity in a vacuum environment [19]. V₂AIC films have a magnification of 25 kX. Figure 2c, f, i shows FESEM images of coated V₂AIC thin films. Regarding the FESEM images, all films' surfaces attract attention with no cracks and show similar morphology. All surfaces are compact and dense without pinholes. AFM images also support FESEM images. The SEM image of Fig. 2c shows fine-grain distribution with low aggregation, indicating homogenous nucleation and development on the substrate. It is also observed that the V₂AIC/ITO/glass film shows greater clustering in places. The images show that the prepared films have a compactly structured, spherical particle shape. Figure 2f shows the SEM image of the branched channels that show continuity during film formation. The SEM images in Fig. 2i demonstrate layered film morphology with differential stratification due to the PET substrate's flexibility and different thermal expansion capabilities [20, 21].

In addition to morphological imaging, surface roughness, grain distribution, skewness (Ssk), and kurtosis (Skr) measurements were performed. Coated V₂AIC surfaces were scanned in the range of $5 \times 5 \mu\text{m}$ in 2D and 3D images of V₂AIC film surface morphologies are depicted in Fig. 2a, b, d, e, g, and h. The grain distribution graph is plotted in Fig. 2j. According to the images, V₂AIC films coated on different substrates exhibited different surface properties. V₂AIC/ITO/glass surface images are irregular cluster-like formations. The 3D AFM images show a smooth surface morphology with a low root-mean-square (RMS) roughness of 19.77 nm, indicating a homogeneously formed thin film on V₂AIC/ITO/glass. Interestingly, V₂AIC/FTO/glass surface images represent regular cluster-like formations and regional agglomerations. AFM images reveal rougher surface morphology, including conspicuous hillocks and an RMS roughness of 274 nm, indicating uneven growth or probable clustering. Finally, V₂AIC/ITO/PET surface images show more distinguishable agglomerations. AFM topography shows intermediate roughness with an RMS value of 86 nm, implying greater control over film production than in the V₂AIC/FTO/glass row but less uniformity than V₂AIC/ITO/glass. Using AFM, all films' root-mean-square (RMS) roughnesses and the symmetric distribution of the crystals were measured. All results are given in Table 2. Skewness (Ssk) and kurtosis (Skr) measurement results provide information about asymmetry and the flatness values on coated film surfaces. If Ssk and Skr values are equal to zero, a perfect symmetrical surface distribution for Ssk and a normal surface distribution for Skr, respectively, will be shown. These results show that V₂AIC/ITO/glass film is better in symmetrical and normal surface distribution than other films. Also, Fig. 2j, according to the height distribution graph, attracts attention to homogeneous grain distribution over the V₂AIC film surfaces. The smallest crystallite size is approximately 9 nm, indicating very nanocrystalline materials. The size distribution is larger, with peaks at around 35 and 86 nm, indicating mixed phase or less regulated growth.

The obtained images showed that the V₂AIC thin films had a smooth and uniform surface shape, indicating homogenous nucleation and growth. The SEM results, i.e., the smoother film exhibiting fine, evenly distributed grains, supported our finding. These findings emphasize the importance of substrate selection and deposition conditions in influencing the microstructure and crystallinity of V₂AIC thin films. This is crucial for maximizing their performance in electrical and flexible device applications.

3.2 Structural properties

The structural characteristics of the coated V₂AIC thin films on the selected substrates are illustrated in Fig. 3. Based on the patterns, the high-intensity peak of the V₂AIC is directly related to the nature of the substrate, which allows the coating process to occur under the same conditions. In the given spectra, the highest intensity peak is V₂AIC, but the films' preferential orientation differed upon ITO/glass, FTO/glass, and ITO/PET substrates, respectively. Due to the lower thickness (200 nm), the substrate-originated peaks also emerged in the patterns. The emerging peaks and their corresponding Miller indices are confirmed in the V₂AIC thin film upon selected substrates. All detailed information about the emerging peaks is listed in Table 3. The magnified peaks were portrayed in the figure to better clarify the peaks.

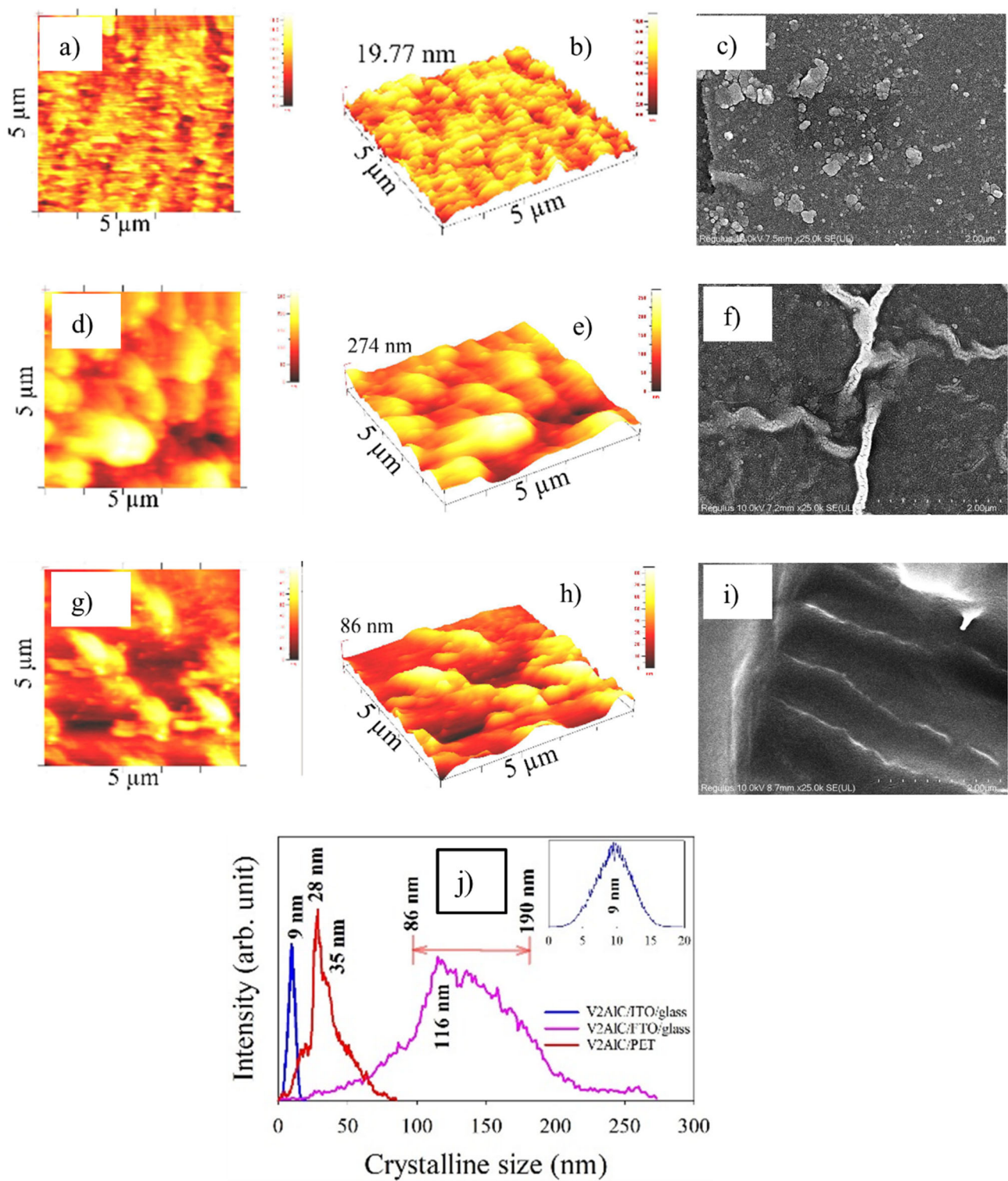


Fig. 2 (a, b) 2D and 3D AFM images of V_2AlC /ITO/glass, (d, e) 2D and 3D AFM images of V_2AlC /FTO/glass, (g, h) 2D and 3D AFM images of V_2AlC /ITO/PET, (c) FESEM image of V_2AlC /ITO/glass, (f) FESEM image of V_2AlC /FTO/glass, (i) FESEM image of V_2AlC /ITO/PET, and (j) crystal size distribution of the V_2AlC films, respectively

Utilizing the patterns, the grain size (GS) [20] of the V_2AlC layer is calculated using the following formula [21]:

$$GS = \frac{0.94\lambda}{\beta \cos \theta} \quad (1)$$

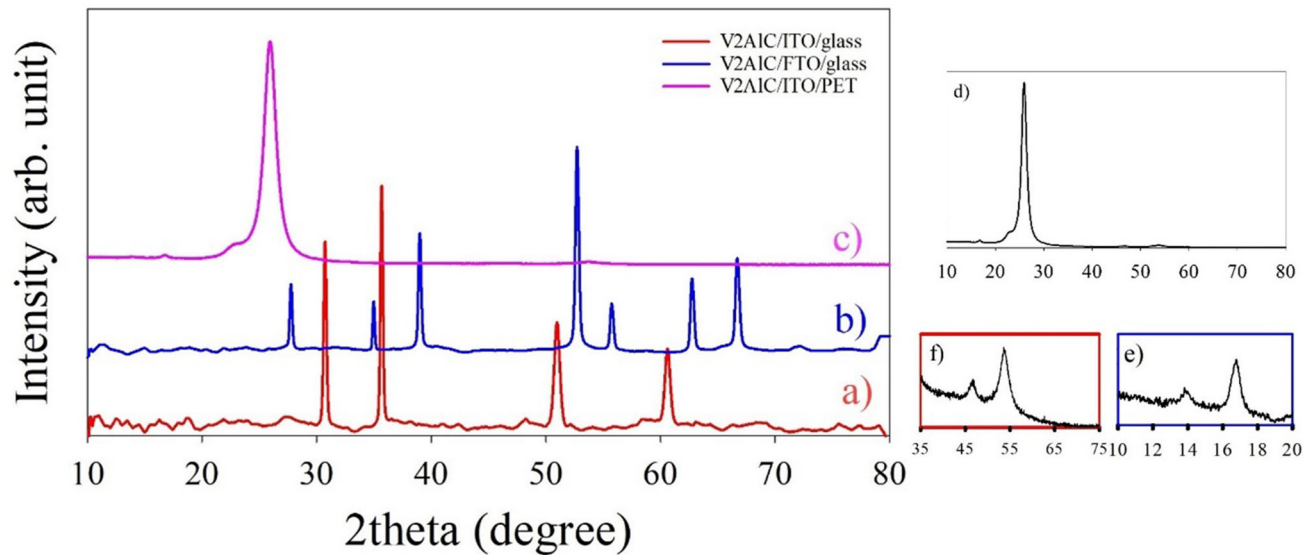


Fig. 3 XRD patterns of the V_2AlC thin films produced upon (a) ITO/glass, (b) FTO/glass, (c) ITO/PET substrates, (d) the magnified preferred orientation of V_2AlC onto the ITO/PET, (e) magnification of the thin films on the FTO/glass, and (f) ITO/glass substrates

Table 3 The results of XRD measurement for the V_2AlC films

	Peak degree	Intensity	Diffraction plane	Phase	GS	δ	ε	Number of crystalline
	(°)	—	—		(nm)	$\times 10^{14}$ (m^{-2})	$\times 10^{-3}$	$\times 10^{15}$ (m^{-2})
V_2AlC /ITO/glass	30.7	451	V_2AlC	114	33	9.3	1.1	5.6
	35.64	633	V_2AlC	100	42	5.8	0.85	2.8
	50.91	269	V_2AlC	105	16	39	2.2	49
	60.57	198	ITO	622	—	—	—	—
V_2AlC /FTO/glass	27.74	265	V_2AlC	004	41	6.0	0.87	3.0
	35.40	267	V_2AlC	100	66	2.3	0.53	68
	38.96	542	SnO ₂	411	—	—	—	—
	52.69	905	V_2AlC		32	9.7	1.1	6.0
	55.71	231	V_2AlC	106	36	7.8	0.99	4.4
	63.72	363	V_2AlC	110	37	7.3	0.95	3.9
	66.66	439	SnO ₂	301	—	—	—	—
V_2AlC /ITO/PET	13.89	495	V_2AlC	002	20	25	1.8	25
	16.76	1704	V_2AlC	101	16	39	2.2	49
	22.62	2547	PET	—	—	—	—	—
	25.92	112,534	V_2AlC	116	19	27	1.8	290
	46.68	1436	V_2AlC	104	8	150	4.4	380
	53.7	2159	—	—	—	—	—	—

herein, the β and θ are the full width at half maximum (FWHM) and the angle of the X-ray diffraction during the measurement, respectively. In the formula mentioned earlier, λ is the X-ray wavelength equal to 0.15405 nm. By considering the GS values, the dislocation density (δ) and micro-strain (ε) during coating are evaluated by the underlying formula [22]:

$$\delta = (GS)^{-2} \quad (2)$$

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad (3)$$

and the number of crystalline per unit area (NC) of the layer after the coating procedure is computed by the following formula [22]:

$$NC = \frac{\text{thickness}}{(GS)^3} \quad (4)$$

in the above formula, the thickness of the layer is measured as 200 nm for all substrates via optical-based measurements.

The results show that the orientation of the diffraction peak is highly affected by the substrate used before the coating process. This issue also directly depends on the PET and glass substrates. Considering the same thickness and similar ITO layer utilized in both cases, the intense peak that emerged in ITO-based V_2AlC thin films is utterly different in orientation and intensity. By considering the same coating parameters, however, the grain size of the V_2AlC layers depends on the nature of the substrate again. Considering the same situation during coating and applying similar parameters, it was concluded that an intense diffraction peak highly influenced the substrate and exploited the conductive layer. Conversely, this condition was governed by the defect-type results. This means the defect values are higher for the V_2AlC layer on ITO/PET. Conversely, the minimum defect was calculated for the V_2AlC -coated ITO/glass substrate. In this study, the grain size ranges from 16–42 nm, 32–66 nm, and 8–20 nm for V_2AlC thin layers upon ITO/glass, FTO/glass, and ITO/PET substrates, respectively. The thin films coated on the glass-based substrate shift toward a lower diffraction (i.e., $35.64 \rightarrow 35.40^\circ$) angle, demonstrating compressive stress during the coating procedure [23].

3.3 Compositional assay

The prepared thin films' element states and surface composition upon the overall substrates were measured via energy-dispersive X-ray spectroscopy (XPS). The high-resolution XPS (HRXPS) and deconvolution of the emerged elements are individually depicted in Fig. 4. In all the survey figures (Fig. 4a, b, c), there are V2p, C1s, Al2p, and O1s peaks [24, 25]. Furthermore, extra peaks such as Na, Ca, Si, and In exist in the figures originating from the conductive layer or the primary substrate. Using HRXPS and in the V2p case, the peak centers are located at 514, 517, and 519 eV, which are attributed to the V-C (2p_{3/2}), V-C (2p_{1/2}) [26], respectively. Additionally, some peaks emerged at 515, 521, and 523 eV correlated with V6O13 (2p_{3/2}), V2O5 (2p_{1/2}) [26], respectively. In the C1s spectra, the peaks centered at 283, 284, 285, 286, 287, and 288 eV represented C-Al, C-C, C-H, C-O, O-C=O, and C=O, respectively [25–27], while in the Al2p element, the peaks deconvoluted at 72, 73, 74, and 75 eV are reflected Al-Al, Al-C, and Al-O, respectively [24, 27].

3.4 FTIR

The technique is a proper analytical method for identifying the distinctive functional groups of the samples and investigating the vibrational characteristics of molecular bonds. PerkinElmer Spectrum Two Fourier Transform Infrared (FTIR) Spectroscopy: A spectrometer was used to analyze the FTIR spectra. With a spectral resolution of 4 cm^{-1} , absorbance spectra covering the frequency range of $4000\text{--}400\text{ cm}^{-1}$ were acquired at room temperature. The background spectra were recorded with the corresponding KBr. The structural alterations and bond stretching of the coated V_2AlC were analyzed using FTIR. The spectra of the coated V_2AlC thin films are shown in Fig. 5a. The figure illustrates that the FTIR spectra of the coated V_2AlC on the various substrate samples are carried out from $4000\text{ to }400\text{ cm}^{-1}$ wavenumber. The peak positions appear reasonably comparable, with the same number of bonds at the same frequencies. The stretching vibrations of the hydroxyl group (–OH) are seen as a broadband at $3300\text{ to }3800\text{ cm}^{-1}$ [28, 29]. We can also see that the medium band at $2902\text{ and }2989\text{ cm}^{-1}$ is attributed to the C-H symmetrical stretching [30]. Additionally, the presence of caused new peaks at broadband $2100\text{ and }2400\text{ cm}^{-1}$ associated with C=C to arise in the stretching vibration modes for the coated V_2AlC thin films. The presence of peaks at $1451, 1409, 1394, \text{ and }1343\text{ cm}^{-1}$ is associated with C–O group stretching [30]; we can conclude that the stretching vibration of V=O bonds is responsible for the absorption bands in the $1025\text{--}900\text{ cm}^{-1}$ range. The stretching vibration of the V=O bond is responsible for the bond at 1066 cm^{-1} . Also, V=O stretching vibrations are related to the bond at 879 cm^{-1} [31]. These are expected values that align with the literature.

3.5 Raman spectroscopy

Raman microscopy was employed to investigate the vibrational properties and band structure of the V_2AlC thin films. A Renishaw inVia Raman Microscope (UK) equipped with a 532-nm laser excitation source and a 2400 l/mm grating was used for the measurements. To prevent localized thermal degradation or oxidation, the laser power was maintained at 5% with an exposure time of 10 s, capturing data across a spectral range of $400\text{--}4000\text{ cm}^{-1}$. Figure 5b shows the deposited V_2AlC films' Raman spectra, which show clear substrate-dependent changes. Characteristic peaks in the $115\text{--}130\text{ cm}^{-1}$ range confirm the primary V_2AlC MAX phase, which is in line with the literature [32, 33]. Every sample has a noticeable peak that is centered at 122 cm^{-1} and is attributed to the E_{2g} mode. This mode is an important indicator of the long-range structural order of the $M_{n+1}AX_n$ stacking and reflects the in-plane shear vibrations of the vanadium (V) and aluminum (Al) atoms within the hexagonal lattice [33–35]. The underlying substrates (ITO, FTO, and PET) have a major impact on the spectral profile. The high-frequency optical modes (w_3, w_4) of the V_2AlC structure, namely V-C stretching vibrations, and the distinctive metal-oxide (Sn–O/In–O) vibrations of the conductive layers are combined to produce the characteristics seen in the ITO and FTO-coated glass samples approximately $556\text{--}561\text{ cm}^{-1}$ [36, 37]. This spectral overlap demonstrates that the Raman probe can detect both substrate signals and intrinsic carbide vibrations due to the thin layers' semi-transparency. Similarly, the symmetric stretching vibrations of Si–O–Si bonds inside the amorphous silica network of the glass substrate are responsible for the strong, broad bands in the $1094\text{--}1099\text{ cm}^{-1}$ range. For the V_2AlC /ITO/PET film, the peak at 637 cm^{-1} is designated as an optical vibration mode (w_{opt}) of carbon (C) atoms within the vanadium (V) octahedra [19].

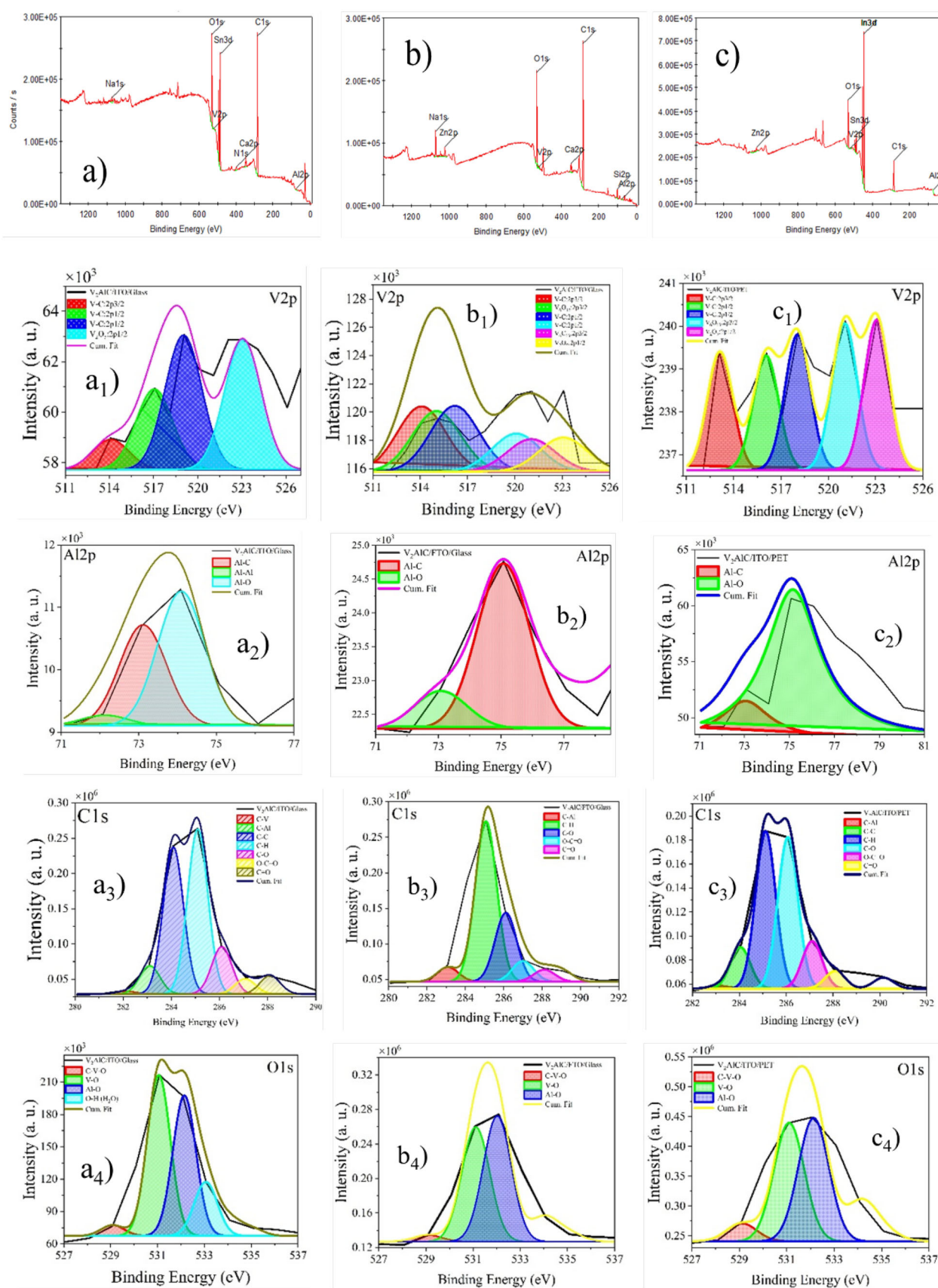
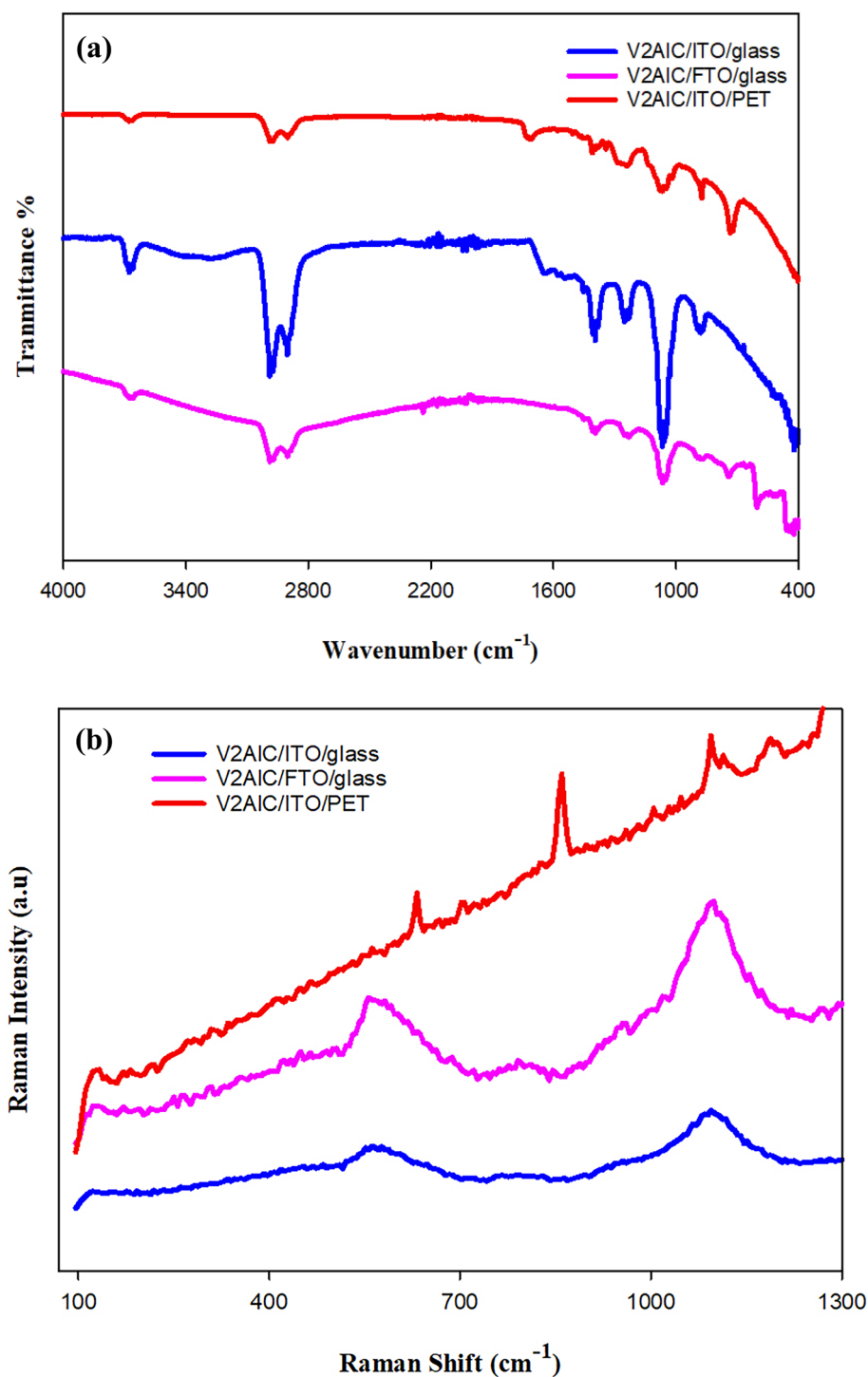


Fig. 4 The XPS and high-resolution XPS (HRXPS) patterns of V_2AlC thin layer on the substrates, (a) $V_2AlC/ITO/glass$, (b) $V_2AlC/FTO/glass$, (c) $V_2AlC/ITO/PET$, a₁, b₁, c₁) V_{2p} , a₂, b₂, c₂) Al_{2p} , a₃, b₃, c₃) C_{1s} , and a₄, b₄, c₄) O_{1s} deconvolution spectrum

Fig. 5 (a) FTIR and (b) Raman spectrum's of the V_2AlC thin layers prepared upon conductive substrates



Unlike low-frequency metal–metal modes, this higher-frequency peak confirms the covalent-ionic character of the M-X (V-C) bonds, validating the purity of the deposited carbide phase. Characteristic signatures of the PET substrate are also evident at 1188 cm^{-1} and 1285 cm^{-1} , corresponding to ester and intra-ring vibrations, respectively. Furthermore, the feature at approximately 859 cm^{-1} suggests V–O stretching vibrations, likely arising from a thin native oxide layer (V_xO_y) or localized laser-induced heating [38, 39]. However, the V_2AlC characteristic modes' dominance at lower wavenumbers indicates that the core structure is still mostly contained within the MAX phase. In summary, low-wavenumber data effectively confirm the structural integrity of the V_2AlC phase, whereas high-wavenumber peaks represent substrate and secondary oxide phases.

3.6 Optical properties

The optical-based measurement of the coated V_2AlC thin films is shown in Fig. 6. Regarding to the results and at the given wavelength, the transparency of the films was recorded as 38, 58, and 44% for the V_2AlC films coated upon ITO/glass, FTO/glass, and ITO/PET substrates, respectively. This result differed for the samples in the same order, that is, 43, 65, and 48% in the visible region (400–700 nm), respectively. In the meantime, the transparency of the deposited thin films is higher in the visible region. This behavior is not related to the nature of the substrates. A reverse relation was also detected for the film's absorbance spectrum. Respecting the measurement results, the FTO substrate causes higher transparency than the ITO substrate. The primary and significant reason for the lower transparency of the prepared thin films may be scattering and reflection from the surface of the V_2AlC [40], grain orientation, and grain sizes. In all samples, interference patterns revealed homogeneity and uniformity [41] of the thin layers.

The prepared layer's reflectance was measured via optical devices. This factor corresponds to the surface attribution into the optical area. Significantly, the ability of the V_2AlC surface to reflect light is abbreviated as reflectance. These spectra are illustrated in Fig. 6c. Regarding the spectra, the reflectance values are directly changed by wavelength. This optical parameter indicates the electronic polarizability of ions in the local field in the V_2AlC . This parameter variation is vital for application areas such as switches, filters, and modulators [42]. In our case, due to the higher amount of reflection, using V_2AlC in the anti-reflective coating is not favorable. The lower roughness of the V_2AlC thin films on the ITO/glass substrate also reduced the reflection value.

The Urbach energy (E_u) of the coated V_2AlC thin films was calculated as below [43, 44]:

$$\alpha = \alpha_0 \exp\left(\frac{hv}{E_u}\right) \quad (5)$$

$$\ln(\alpha) = \ln(\alpha_0) + \left(\frac{hv}{E_u}\right) \quad (6)$$

herein, α_0 is a constant value, hv is a photon energy, and the following formula computes α [45]:

$$\alpha = 2.303(\text{absorbance}/\text{Thickness}) \quad (7)$$

The Urbach energy values of the coated V_2AlC thin film were 251 and 249 meV on the ITO and FTO-coated glass substrates, respectively, and 217 meV for the film on the ITO/PET. This value is obtained by calculating the $\ln(\alpha)$ inverse slope versus hv . Indeed, Urbach energy recognizes the variation in the band gap value of the prepared film. An increasing E_u value leads to a narrowing band gap [46]. This parameter indicates the availability of structural disorders and defects during the coating process. In terms of the E_u values, in our case, there is a good coincidence between the XRD-based calculation and optical results from a defect and disorder standpoint. However, this parameter significantly and reliably deemed the formation of different crystal orientations in the V_2AlC layer [46]. This issue also negatively affected the electrical properties of the film.

Another optical parameter that describes the thin-film material features is skin depth. The parameter typically accepted the depth that radiation can penetrate the material as a thin film to the $1/e$ (or about 37%) [47] value compared to the surface. Indeed, the absorption of photons through thin film was ascribed to the crystal structure, element distribution, thickness, and nature of a material [48]. Meanwhile, the parameter attributed to the optical conductivity of the thin film produced is inversely related to the absorption coefficient (α). The skin depth was generally demonstrated according to the below formula:

$$\text{Skindepth} = \frac{2}{\alpha} \quad (8)$$

The skin depth spectrum of the coated films is depicted in Fig. 6g. By increasing the radiation value, the skin depth tends to minimum value and finally achieves zero value. The zero point is well-known as the cutoff point, meaning cutoff wavelength or cutoff energy. In this research, the cutoff energy values are obtained as 4.3 ($\lambda_{\text{cutoff}}=288$ nm), 4.35 ($\lambda_{\text{cutoff}}=285$ nm), and 3.97 eV ($\lambda_{\text{cutoff}}=312$ nm) for V_2AlC deposited upon ITO/glass, FTO/glass, and ITO/PET substrates, respectively.

3.7 Electrochemical properties

The electrochemical features of the prepared thin films regarding the substrate are depicted in Figure 7. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out to evaluate the performance, kinetics, mass transport, charge transport, and equivalent circuits of the samples. Figure 7 illustrates the potential versus current density by considering the scan rate. Respecting the curves, the CV results can be classified into two groups. This behavior is likely owing to the films' various preferential crystal configurations. The V_2AlC thin film prepared onto the ITO/glass substrates demonstrated Faradic and reversible reactions [33]. On the other hand, the film coated on either FTO/glass or ITO/PET substrates demonstrated non-Faradaic or capacitive behavior. For the film upon ITO/glass, there are a couple of oxidation and reduction peaks that possibly give rise to the crystalline nature of the film besides the substrate. This case confirmed the pseudocapacitive features of the film upon the ITO/glass substrate. Similar conditions were already reported by M. S. Mohseni-Salehi [33]. This result demonstrated the suitability of the prepared film for capacitor and ion-type batteries. The area inside the CV curves obeyed the scan rate, i.e., this relation is in a direct mode. In all cases, the scan rate value enhanced the minimum and maximum current density values at each curve at the edge of potential

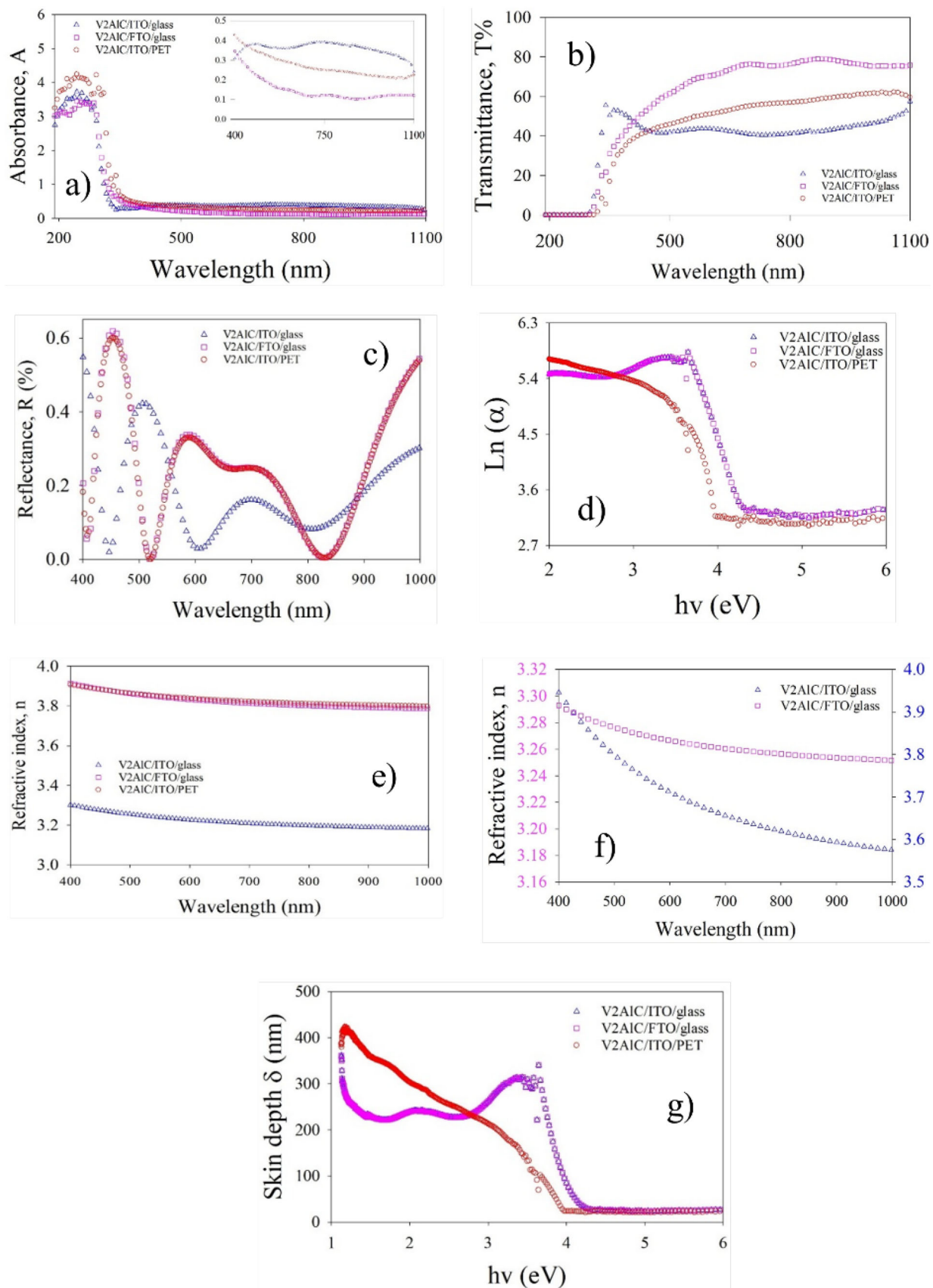


Fig. 6 (a) The absorbance, (b) transmittance, (c) reflectance, (d) Urbach energy, (e) refractive index, (f) zoom-in refractive index, and (g) skin depth distribution of the deposited thin film onto the selected substrates

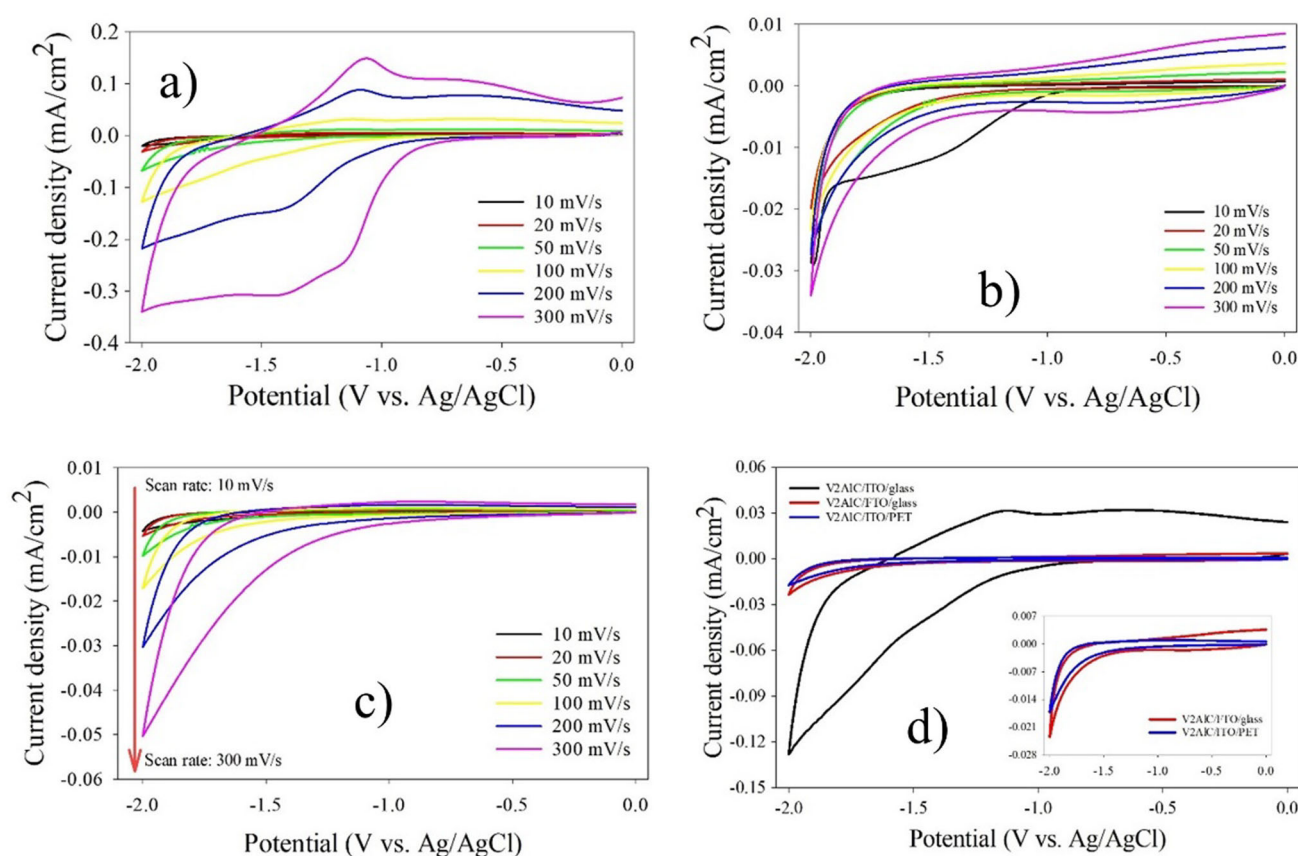


Fig. 7 The cyclic voltammetry analysis results versus different scan rates for V_2AlC thin films coated on (a) ITO/glass, (b) FTO/glass, (c) ITO/PET, and (d) comparison of the CV curves for all samples at 50 mV/s scan rate

windows. Particularly in the ITO/glass substrates, the lithium-ion storage of the V_2AlC layer was dramatically elevated in order to increase the CV curve area.

The dominant reaction is non-Faradaic in the films coated upon FTO/glass and ITO/PET substrates. This kind of behavior typically originated from a double layer formed on the film between the working electrode (viz V_2AlC /substrate) and Li-based electrolyte (i.e., $LiClO_4$) [49]. The double layer plays a pivotal role in electrocapacitive charging and discharging against voltage deviation during the cyclic voltammetry experiment [50]. It is worth noting that, generally, in the double-layer mechanism, the specific capacitance of the desired material is delineated according to the surface area. Scanning in a wide potential window revealed high stability against the degradability of the films during the intercalation/de-intercalation of Li-ion into the structure.

By comparing the CV cycles in the same scan rate, the highest area inside the test was achieved for V_2AlC film deposited upon the ITO/glass substrate. This result may be due to the film's crystalline nature, substrate, and morphological variation. Meanwhile, in the CV data, for all cases, the increase in the minimum and maximum of the edge apex is associated with the enhancement of H ions into the film, which leads to reactivity improvement [51].

The films' impedance and conductivity were simulated via equivalent circuit elements. Taking the crystalline behavior of the films and variants in the substrate into account, two different models were fitted with the Nyquist curve (Fig. 8f). The values of successful fitted elements are outlined in Table 4. In all cases, R_s , R_{ct} , and constant phase element (CPE) represent electrolyte–electrode interface resistance, charge transfer resistance, and diffusion at the low-frequency region, respectively. The magnified electrochemical impedance spectroscopy of the films upon ITO/glass and FTO/glass substrates is depicted in the figure's inset.

A constant phase element (CPE) was introduced into the circuit to fit the model well. This element indicates chemical diffusion that is attributed to non-ideal performance; meanwhile, the non-uniform distribution of current is in our prepared films [52]. The main formula for CPE is [43]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (9)$$

in the above formula, Y_0 stands for the admittance of an ideal capacitor, and n is extended from 0 to 1 (i.e., $0 < n < 1$). If the n value equals 0, then the CPE element shows resistance. In contrast, if the value is equal to 1, and in the case of $n=0.5$ associated with the Warburg element, it confirms capacitor behavior. In this research, the films coated upon ITO/PET show more pure capacitive

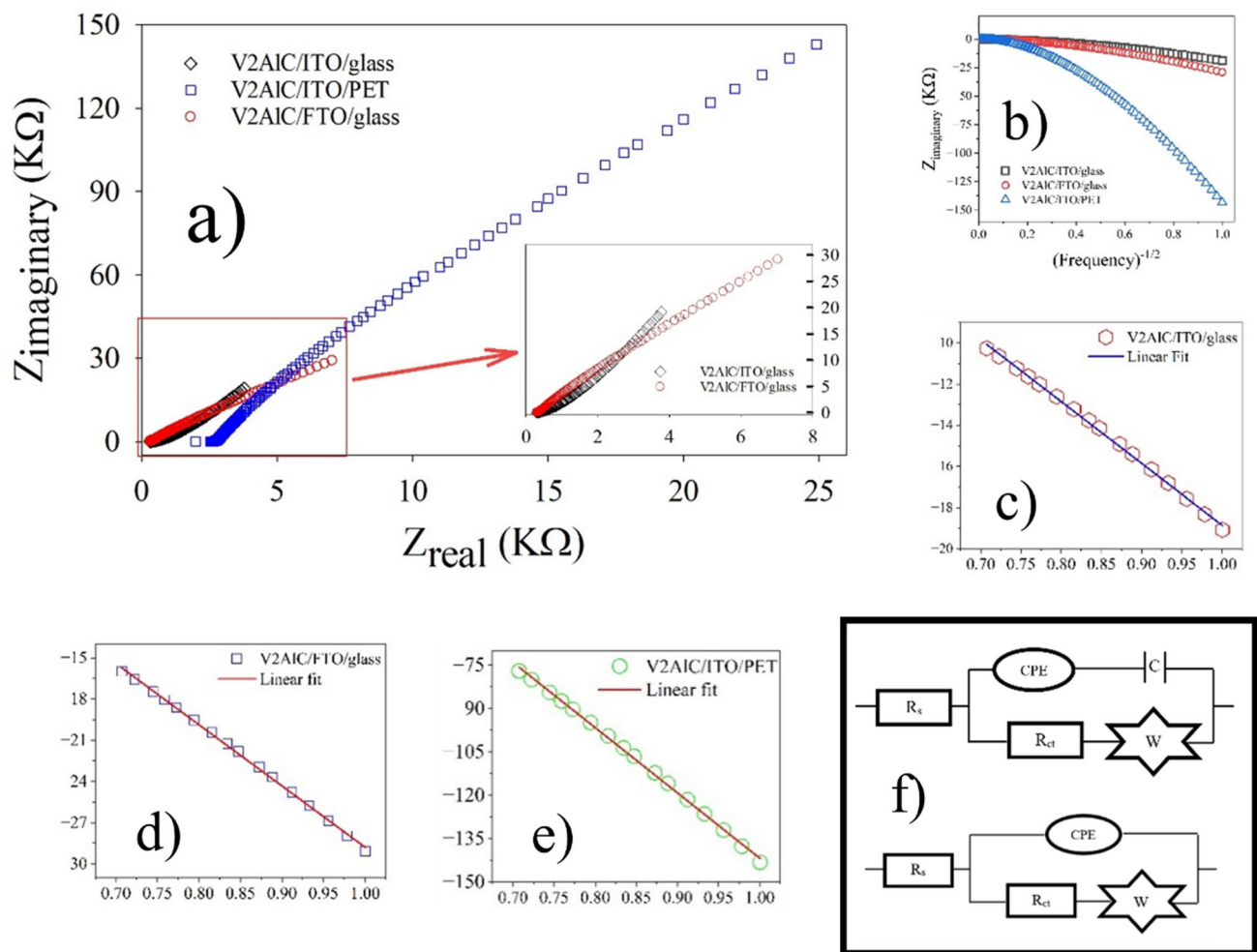


Fig. 8 (a) The electrochemical impedance spectroscopy (EIS) curve of entire samples, (b) Z_{imag} versus $\nu^{-1/2}$, (c, d, e) slope of the linear part of the Z_{imag} versus $\nu^{-1/2}$ or Warburg coefficient, (f) equivalent circuit for the samples

Table 4 The calculated value of the equivalent circuit of the samples after well fitting

		V ₂ AIC/ITO/glass	V ₂ AIC/FTO/glass	V ₂ AIC/ITO/PET
Parameters	Unit	Values	Values	Values
R_s	Ω	302	323	2635
R_{ct}	$M\Omega$	1	30	40
W	$M\Omega s^{-0.5}$	9	40	2
Y_0	$\times 10^{-6}$	60	6	1
n	—	0.58	0.88	0.94
C	μF	10	—	—

behavior in the low-frequency region. This behavior originated from the tail angle of the Nyquist curve in the low-frequency region. In the high-frequency zone, the intercept of the curve and the Z_{real} axis indicate R_s . This value is much higher for the film prepared upon the ITO/PET substrate.

In the electrochemical impedance analysis, the resistance series were ordered according to the below equation [53]:

$$Z_{\text{real}} = R_s + R_{ct} + \sigma_w \omega^{-0.5} \quad (10)$$

herein, the diffusion coefficient of the electrolyte, i.e., Li-ion into the host material, is evaluated by the underlying formula [43]:

$$Z_w = \sigma_w (1 - j) \omega^{-1/2} \quad (11)$$

The Li-ion diffusion coefficient can be easily obtained by fitting the linear part of the $Z_{\text{imaginary}}$ versus $\omega^{-1/2}$ in a low-frequency region. Also, σ_w pointed out the Warburg coefficient [45], in this analysis, which is computed by the slope of the linear fitted section of the curve. In the $V_2\text{AlC}$ prepared upon different substrates, the Warburg coefficient of the layer was obtained as 0.04×10^6 , 0.03×10^6 , and 2×10^6 upon ITO/glass, FTO/glass, and ITO/PET substrates, respectively. Compared with our recently published paper, which glassy-based amorphous thin film prepared with a similar coating technique [45], the Warburg coefficient in $V_2\text{AlC}$ thin film was highly promoted by 6, 4, and 29-fold. This improvement in the $V_2\text{AlC}$ indicates this type of MAX series's high suitability, reliability, and capability for further exploration as a good candidate for storage applications. In the low-frequency region, after diffusion of enough Li-ion into the structure, the coated layer adopted to show capacitive behavior except for porous properties of the layer hindered this behavior [54]. The parameter is prominently inferred as mass transport in the low-frequency region in the electrolyte.

4 Conclusion

The TVA technique was used to coat 200-nm-thick $V_2\text{AlC}$ thin films produced on three different conductive and two-structure variant substrates. Then, by investigating the physical and electrochemical properties, an X-ray examination revealed that the $V_2\text{AlC}$ thin films have a crystallite structure. Further, the Raman and FTIR measurements supported the successful formation of the $V_2\text{AlC}$ structure. The morphological parameters proved smaller roughnesses, homogeneity, compactness, crack-free, and symmetrical distribution of the particles upon the selected surface. Compositional patterns coincide with the structural results, i.e., indicating the existence of V, Al, and C bonds in our case. Regarding the Urbach energy values, the defect structure was reduced in $V_2\text{AlC}/\text{ITO}/\text{PET}$ specimen.

The CV and EIS properties of films were also investigated. In terms of the electrochemical measurements, the cyclic performance and behavior of the $V_2\text{AlC}$ layers varied in order to substrate and conductive layer properties. However, the thin layer coated onto the ITO/glass shows oxidation–reduction peaks against Li-based electrolyte. On the other hand, using the same electrolyte, no oxidation–reduction peaks exist in the thin film prepared upon FTO/glass and ITO/PET substrates. In other words, the CV curves demonstrated non-Faradic behavior in this case. Additionally, by comparing the cyclic voltammetry curves, the $V_2\text{AlC}/\text{ITO}/\text{glass}$ specimen presented higher capacitance, choosing the same scan rate and same conditions.

Based on this work, it was obviously specified that the $V_2\text{AlC}$ thin films could be used for advances in Li-ion batteries, capacitors, and sensors prepared with physical vapor deposition techniques.

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Data availability All data generated or analyzed during this study are included in this published article.

Declarations

Conflict of interest The authors stated that they have no known competing financial interests or personal relationships that could have appeared to affect the research reported in this paper.

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