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Blue- and red-shifts of V$_2$O$_5$ phonons in NH$_3$ environment by *in situ* Raman spectroscopy

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Abstract

A layer of ~30 nm V$_2$O$_5$/100 nm-SiO$_2$ on Si was employed in the *in situ* Raman spectroscopy in the presence of NH$_3$ effluent from a thermal decomposition of ammonium acetate salt with the salt heated at 100 ºC. When the layer is placed at 25 ºC, we observe a reversible red-shift of 194 cm$^{-1}$ V$_2$O$_5$ phonon by 2 cm$^{-1}$ upon NH$_3$ gas injection to saturation, as well as a reversible blue-shift of the 996 cm$^{-1}$ by 4 cm$^{-1}$ upon NH$_3$ injection. However when the sensing layer is placed at 100 ºC, the 194 cm$^{-1}$ remains un-shifted while the 996 cm$^{-1}$ phonon is red-shifted. There is a decrease/increase in intensity of the 145 cm$^{-1}$ phonon at 25 ºC/100 ºC when NH$_3$ interacts with V$_2$O$_5$ surface. Using the traditional and quantitative gas sensor tester system, we find that the V$_2$O$_5$ sensor at 25 ºC responds faster than at 100 ºC up to 20 ppm of NH$_3$ beyond which it responds faster at 100 ºC than at 25 ºC. Overall rankings of the NH$_3$ gas sensing features between the two techniques showed that the *in situ* Raman spectroscopy is faster in response compared with the traditional chemi-resistive tester. Hooke’s law, phonon confinement in ~51 nm globular particles with ~20 nm pore size and physisorption/chemisorption principles have been employed in the explanation of the data presented.

Keywords: V$_2$O$_5$, VO$_2$, *in situ* Raman sensing, blue-shift, red-shift, selectivity, phonons

Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductor metal oxide gas chemo-resistive sensors have been a preferred transduction or method of detecting flammable, combustible, poisonous and toxic gases for many years. Now, since its inception in 1960, when scientists discovered changes in the conductivity of semiconductor materials in the presence of gas and air [1–3], chemo-resistive technique has been a major means of transducing chemical and physical signals by converting them into a measurable one. Among other modern gas sensors or transducers such as electrochemical [4], optical [5], acoustic [6]; the metal oxide chemi-resistor is more applicable in real-life practical devices due to the characteristics such as low cost, long lifetime, fast response...
time and high sensitivity [3]. However, the ability to selectively adsorb or detect a certain species or type of gas/analyte has been the limiting factor constraining the reliability of metal oxide chemi-resistors in critical application areas like environment monitoring, health diagnosis, automotive, space exploration, biomedical and pharmaceutical etc.

Raman spectroscopy is a reliable, sensitive and non-destructive method used in characterizing metal oxides and other nanomaterials [7, 8]. The Raman technique has been applied to study adsorption of molecules on the surface of metal oxides and to monitor their selective ability toward certain species of gas [9–11]. Among these studies, $A_{1g}$ mode of SnO$_2$ was observed to show a huge enhancement when H$_2$S gas reacted with Cu doped SnO$_2$ nanomaterial [9]. This enhancement is observed to be absent when the material is exposed to air. The effect is reported to be reversible and the band is attributed to Cu$_2$S vibration, thus showing reactivity of Cu doped SnO$_2$ with H$_2$S. Nanocrystalline WO$_3$ powder has also been found to react with the reducing gases CH$_4$ and CO resulting in the growth of two broad band peaks at 1300 cm$^{-1}$ and 1600 cm$^{-1}$ which were observed to be absent in the Raman spectrum of pure WO$_3$ [10, 11]. Whereas, these peaks disappeared in the presence of an oxidizing gas NO$_2$ and thereby are attributed to the graphic carbon peak usually present in many carbon materials [7]. This showed reactivity of CH$_4$ and CO with the WO$_3$ surface. Vanadium oxides materials are very sensitive to Raman spectroscopy [8, 12, 13] and are often characterized by it to explore their structural, metal-insulator and nanostructured properties [8]. The reason for this sensitivity is nothing less than the vanadium oxide’s variation in its oxidation state and crystallographic structures which usually cause atomic or lattice displacement (distortion), causing active vibration [8, 12–18].

Vanadium pentoxide with a generic name (V$_2$O$_5$) and its vanadium oxides (V$_2$O$_3$, V$_2$O$_5$, V$_3$O$_7$, etc) has been widely used for gas sensing due to its semiconductor and thermodynamic properties and atomic arrangement in the crystallographic unit cell [8, 12–18]. This material including VO$_2$ with V$^{5+}$ ionic state, has been extensively applied for applications such as solar window, smart window; e.g. thermo-chromatic and electrochromic devices, anti-reflecting coatings and lithium ion battery [12, 13, 17, 18]. V$_2$O$_5$ macroscopic structure (bulk), nanostructure and the one whose radius is comparable with Debye length is thermodynamically favoured as orthorhombic unit cell at ambient conditions. This compound has the highest oxygen concentration among other vanadium oxide members; its crystallographic atomic arrangement provides room for corner-sharing and edge-sharing VO$_5$, octahedral geometry with space group $D_{2h}^{13}$ $Pmnm$ (No. 59) layered structure and lattice parameters $a = 11.510$ Å, $b = 3.563$ Å and $c = 4.369$ Å where $b$ and $c$ are frequently interchanged in orthorhombic system [17, 18]. According to the international crystallographic tables and density functional approximation records [17, 18], stoichiometric orthorhombic V$_2$O$_5$ structure should have four types of atoms in terms of their geometry coordination i.e. by their nature of bonding and bond length. One vanadium atom V and three different oxygen atoms O (1), O (2) and O (3) located at different Wyckoff positions. V atom together with O (1) and O (3) occupy 4f/Wyckoff position with site symmetry C$_s$ whereas O (2) atom can occupy 2a/Wyckoff position with site symmetry of C$_2$ [18, 19]. High symmetry orthorhombic lattice of V$_2$O$_5$ crystal structure with two formula per unit cell contains a total of 42 optical and acoustic modes. Among these 42 modes, three ground state modes are acoustic with zero frequency at high symmetry point called Γ-point.

The first order Raman active modes of this structure can be obtained from the symmetrized square of the vector representation $(x,y,z)$ as the second rank polarizability tensor in the space group $D_{2h}^{13}$ with 8 symmetry elements namely; $E$, $C_2(z)$, $C_2(y)$, $C_2(x)$, $i$, $σ(xy)$, $σ(xz)$ and $σ(yz)$ and by factor group analysis and selection rule for $D_{2h}^{13}$ point group. The infrared modes transform as $(x, y, z)$ representation, since they are related to the electric dipole moment. Zhou et al [19] reported that 21 Raman active modes composed of $A_{1g}$, $B_{1g}$, $B_{2g}$ and $B_{3g}$ modes may be present in the V$_2$O$_5$ crystal while the remaining 18 modes may be due to infrared absorption (i.e. infrared active). On the other hand, the low temperature phase of VO$_2$ structures has space group $P2_1/c$ (No. 14) and two atoms per unit cell in monoclinic crystal system. Group theory predicts 18 total modes and 15 optical zone-centre modes at wave vector $q = 0$ in the Brillouin zone (at Γ-point) from lattice mode representation by acting four symmetry elements $E$, $C_2(z)$, $i$ and $σ(xy)$. These modes composed of $A_{1g}$, $B_{1g}$, $B_{2g}$ and $B_{3g}$ which were distributed in different configurations with respect to the crystal structure of the precursor compound. In this paper, we identify these vibrational modes in in situ Raman spectra of the V$_2$O$_5$ surface as it interacts with the NH$_3$ molecule as predicted from group theory. The study combined Raman spectroscopy methods, group theoretical approaches and electrophysical techniques to show the reactivity of vanadium oxide surface to NH$_3$ molecule at ambient temperatures and at 100 °C by oxygen iono-sorption and lattice vibration mode assignment. The set-up could be miniaturized to find its usefulness in portable sensitive and selective chemical sensors or applied as a stationary industrial gas detector.

2. Theoretical considerations

This section includes some science of how Raman scattered photon population from a typical nanostructured surface is affected by the presence of reducing or oxidising gases. In this regard, one can use a number of basic theories providing the intensity, $I$, of Raman scattered photons as a function of surface characteristics. One of the most appropriate theories is the phonon confinement models generally given by [20–24].

$$I(ω, q) = A_0 \int_0^∞ \frac{exp \left(-ωq^2\right)}{[ω - ω(q)]^2 + (Γ_0/2)^2} dq$$ (1)

where $q$ is the wave vector in the Brillouin zone, $ω(q)$ is the phonon dispersion relation for the material, $α$ is the scaling factor, $Γ_0$ is the full-width-at-half-maximum broadening of the Raman peak, and $A_0$ is the proportionality constant. The integral is performed over all ranges of the wave-vector, $q \sim 0$, which is further proportional to $πα/λ$, where $λ$ is the
laser wavelength and \(a\) is the lattice parameter of the material. Any change in \(I(\omega, q)\) should be due to less or more Raman scattered photons which means less or more phonons in the surface. This is a further signalling indicator of the chemical interactions or reactions that happen in presence of reducing or oxidising gases. The change in intensity of Raman scattered photons or phonons can be found by differentiating equation (1) with respect to both variables as follows

\[
dI = A_0 \frac{\partial}{\partial \omega} \left( \int_0^\infty \frac{\exp(-\alpha q^2)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} dq \right) \bigg|_\omega d\omega + A_0 \frac{\partial}{\partial q} \left( \int_0^\infty \frac{\exp(-\alpha q^2)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} dq \right) \bigg|_\omega d\omega.
\]

(2)

The first term in equation (2) gives the number of phonons of varying wavenumbers confined in the nano-particle but can only be evaluated numerically. The first part of equation (2) reduces to zero as a differential with respect to \(\omega\) for the case when \(\omega\) does not change, as will be seen in the experimental section this yields to null. The second term, however, can be simplified and equation (2) can then be re-written as

\[
dI = A_0 \frac{\exp(-\alpha q^2)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} \left( \frac{2q\alpha [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2 + (\Gamma_0/2)^2 + [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2}{2q\alpha [\exp(-\alpha q^2)]^2 (\Gamma_0/2)^2 + [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2} \right) \bigg|_\omega d\omega.
\]

(3)

In terms of the response defined from the changes in Raman peak heights and their changes, it is appropriate to evaluate the fractional change of intensity rather than merely change in intensity. The latter suffers from variations from spot to spot. Therefore, in this study we define Raman intensity response as a fractional change in intensity referenced to the Raman peak height before the analyte gas is introduced as follows:

\[
\frac{dI}{I} = \frac{\exp(-\alpha q^2)}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2} \left( \frac{2q\alpha [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2 + (\Gamma_0/2)^2 + [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2}{2q\alpha [\exp(-\alpha q^2)]^2 (\Gamma_0/2)^2 + [\exp(-\alpha q^2)]^2 [\omega - \omega(q)]^2} \right) d\omega.
\]

(4)

When equation (4) is further analysed in terms of the actual sensing, one can reduce it to the following shorthand version:

\[
\frac{dI}{I} = f(q, \omega(q), \omega, \alpha).
\]

(5)

Since \(\lambda\) is a laser wavelength, which is a constant during the Raman spectra acquisition and \(q = 2\pi/\lambda\), then \(q\) is a constant and \(\omega(q)\) is constant. We shall show in the experimental section that \(\omega\) is also a constant. Therefore we can re-write it to

\[
\frac{dI}{I} = f(\alpha).
\]

(6)

The scaling factor \(\alpha\) varies from materials surface to another and also depends on polarization effects apart from the number of phonons interacting with the laser photons. The number of phonons is further affected by the presence of gaseous molecules. This theoretical discussion on Raman peak intensity changes will be discussed further with experimental validation in later section.

It is also very important to discuss the theory of phonon frequency (wavenumber) changes owing to gas interaction with the material surface. There will be blue or red shifts in the vibrational frequencies due to these changes. If one imagines a linear chain model of fundamental frequency \(\omega_2 = \kappa/\mu\), where \(\kappa\) and \(\mu\) are spring constant and reduced mass of the masses on the spring, respectively, then the change in vibrational frequency, \(d\omega\), should be one that depends on both the change in \(\mu\) and \(\kappa\). The change in \(\kappa\) takes place when the number of electrons per bond change, whereas the change in \(\mu\) happens when active gas elements such as oxygen desorbs or adsorbs. These changes can be, mathematically, represented as follows:

\[
\frac{\partial \omega}{\partial \kappa} = \frac{1}{2\sqrt{\kappa/\mu}}
\]

(7)

and

\[
\frac{\partial \omega}{\partial \mu} = \left( -\kappa \mu^2 \right) \frac{1}{2\sqrt{\kappa/\mu}} = \left( -\kappa \mu^2 \right) \frac{\partial \omega}{\partial \kappa}.
\]

(8)

The total change in frequency can be written as

\[
d\omega = \frac{\partial \omega}{\partial \mu} d\mu + \frac{\partial \omega}{\partial \kappa} d\kappa = \frac{1}{2\sqrt{\kappa/\mu}} \left( d\kappa - \frac{\kappa}{\mu^2} d\mu \right).
\]

(9)

So, if \(d\kappa > d\mu/\mu^2\), one expects a blue shift, whereas when \(d\kappa < d\mu/\mu^2\) then one should expect a redshift in the Raman spectra. Both change in intensity of the phonon (equations (1)–(3)) and their frequencies (equations (4)–(6)) will be used to explain the in situ Raman spectra with gas sensing.

3. Experimental

A pulse laser deposition (PLD) technique was employed in this study to grow VO\(_2\) thin film on Corning glass substrates. The glass substrates were rigorously cleaned and rinsed several times (in ethanol and deionized water) with an ultrasonic bath in order to remove impurities and ensure quality. Vanadium oxide (VO\(_2\) nanoparticles (NPs) powder with 99.9% purity) from Sigma Aldrich was converted to pellet using an
ENERPAC P142 hydraulic cold press system made in the USA. About 5 g of VO₂ (NPs) powder was slightly dampened with methanol and transferred into a 20 mm hollow die after which a load of 100 tons was mounted on the specimen, and the resulting pellet was annealed at 500 °C for ~24 h. The set-up and plasma plume dynamics of the PLD system used for this work is similar to the one reported in [25]. Nd:YAG laser beam (λ = 266 nm, τ = 8 ns) was directed to the chamber by the aid of several mirrors and later focused onto the VO₂ pellet target at an incident angle of 45° using two cylindrical lenses. The minimum pulse energy was applied at 45 mJ with laser fluence of 2 J cm⁻¹ and the substrate to target distance of 5 cm was maintained during deposition. Oxygen partial pressure was set to 0.05 mbar (37 mTorr) after evacuating the chamber to the base pressure of 3.1 × 10⁻⁵ mbar, and the film was deposited for 30 min. The x-ray diffraction patterns of the film were measured at room temperature using the Panalytical XPERT PRO PW3050/50 diffractometer with CuKα radiation (45 kV, 400 mA, λ = 0.1540598 nm and 5° ≤ 2θ ≤ 90°). The Auriga ZEISS scanning electron microscope (SEM) was employed to study the morphology of the film and to estimate the thickness of oxide layers that are present. SAXSess Anton Paar small-angle x-ray scattering spectroscopy was employed for the particle size and pore size analysis of the film. High resolution x-ray photoelectron spectroscopy (XPS) was obtained with a PHI 5000 VersaProbe system. A low energy Ar⁺ ion gun and low energy neutralizer electron gun were used to minimize charging on the surface. A 100 µm diameter monochromatic Al Kα x-ray beam (hν = 1486.6 eV) generated by a 25 W, 15 kV electron beam was used to analyze the different binding energy peaks. The pass energy was set to 11 eV giving an analyzer resolution ≤0.5 eV. Multipack version 8.2 software was utilized to analyze the spectra to identify the chemical compounds and their electronic states using Gaussian–Lorentz fits.

Time of flight secondary ion mass spectroscopy (TOF-SIMS) analyses were performed using an IONTOF TOF SIMS® instrument with bismuth 1+ as the primary ion source (30 kV, 1 pA pulsed at 10 kHz). These analyses were carried out in negative secondary ion mode and under ultra-high vacuum (base pressure) of ~10⁻⁹ mbar. A Cesium (1 kV, 75 nA) sputter gun was used. The analysis area was 100 × 100 µm² and the sputter area was 300 × 300 µm² at a resolution of 512 × 512 pixels with a binning of 4 pixels.
Raman structural properties of the film and in situ-sensing measurement of NH\textsubscript{3} effluent produced from ammonium acetate at 100 °C was carried out using a Bruker spectrometer. A Bruker Raman Senterra spectrometer equipped with 50× optical objective and a 532 nm excitation laser, at a laser power of 0.2 mW, was used for accumulating the films’ spectra. The typical experimental set-up of the in situ Raman sensing measurement is presented in figure 1 wherein a 532 nm Nd:YAG laser was directed to the film glued onto an Al\textsubscript{2}O\textsubscript{3}–Pt interdigitated electrode set. The heating terminals of the interdigitated electrode are connected to a DC power supply and the whole specimen is enclosed in a transparent chamber where NH\textsubscript{3} effluent from the thermal decomposition of ammonium acetate was allowed flow through. Conductometric sensing measurements were conducted using KSGA565 KEITHLEY source meter, after which the currents across the film were measured for different concentrations of NH\textsubscript{3} gas.

4. Results and discussion

Figure 2(a) shows the XRD pattern of the film, the pattern shows that the film is predominantly composed of V\textsubscript{2}O\textsubscript{5}, according to the Institute for crystallographic and diffraction database, with a powder diffraction number of (PDF 41-1426).
but with trace phases of VO$_2$ and V$_6$O$_{13}$ according to (PDF 76-0676) and (PDF 27-1318), respectively. This x-ray spectrum has been matched with the Rietveld structure refinement method with the Bragg positions showing strong correlation with the V$_2$O$_5$ structure; this report is given in the supplementary material (SM) (stacks.iop.org/JPhysD/51/015106/mmedia). The average crystallite size $L$ and lattice micro/nano strain $\varepsilon$ of the film were calculated using the well-known Scherrer’s and Williamson–Hall formula (presented in the SM) [26, 27] and were found to be ~70 nm and 0.000651 ± $1.32 \times 10^{-4}$, respectively. Figure 2(b) is the plot of the Williamson–Hall assumption for lattice strain determination. The film morphology are presented in figure 3 with (a) showing the in-plane formation of clusters of particles with pores at the surface and (b) the cross section at the edge of the film showing that the film is ~30 nm in thickness. Figure 3(c) presents a small-angle-x-ray-scattering (SAXS) plot of scattering intensity versus the wave vector for the V$_2$O$_5$ layer. From the software on the SAXS instrument based on Guinier et al.’s formulations, the morphology of the layer is interpreted to be composed of nearly spherical particles from the linearity of the extreme side of the small wave vector and this gives a mean particle diameter of 51.15 ± 0.60 nm. This translates to a surface-to-volume ratio estimated at 8.25 ± 628.60 m$^2$ cm$^{-3}$ estimated at the wave vector of 2 nm$^{-1}$ end of the spectrum. Figure 3(d) presents a differential of the spectrum in figure 3(c) which is derived from the well know intensity–wave vector–radial distance equation [28]

$$I = c \int_0^{\infty} n(r)f(q,r)S(q,r)\,dr$$

where $n(r)$ is the normal particle size distribution curve such as the Gaussian, Lorentzian or lognormal and the like, $f(q,r)$ is the form factor and $S(q,r)$ is the structure factor. For materials without dopants like in our present case, the form factor is unity and similarly the structure factor. Therefore, a differential of the $(q,I)$ data with respect to $q$ of equation (10) gives a plot of the $S$-curve type as given in figure 3(d). When a Boltzmann’s $S$-curve equation is fitted to the differential curve, the central $q_0$ and its standard deviation are found to be 0.06 ± 1.58 $\times 10^{-4}$ which when converted from the reciprocal space, $q$, to the real space, $r$, gives the mean diameter, $r_0$, of about 50 nm which confirms the software-obtained value of the particle size. We can conclude the average particle size by SAXS to be 51 nm for this 30 nm layer which, when hexagonal close packing of these particles is considered, forms pores of mean diameter of about 20 nm. Phonon confinement is therefore possible because of the tight pore size rather than particle size.

![Figure 5](image-url)
XPS spectrum of the surface of the V$_2$O$_5$ film is represented in figure 4 with (a) displaying the overall core level XPS survey spectrum and (b) showing Lorentzian–Gaussian deconvoluted core level spectrum of V-2p and O-1s for the V$_2$O$_5$ film. The $\frac{1}{2}$ spin–orbit doublet component of the V-2p photoelectron was found to be 524.9 eV for V$_{4}^+$ and 523.6 for V$_{5}^+$ state while the 3/2 spin–orbit component after further Lorentzian- Gaussian dividing peak analysis gives 517.25 and 516.2 eV for V$_{5}^+$ and V$_{4}^+$ respectively [29, 30]. The oxygen O1s is deconvoluted into three peaks, 531, 533 and 535 eV which can be assigned to adsorbed oxygen (a), single bonded oxygen (b) and double bonded oxygen (c) respectively. The TOF SIMS measurement has been used to unveil the chemical elements that are present in V$_2$O$_5$ film as a function of sputter-depth, the results are presented in figure 5 where (a) shows depth profile of the negative ions of V, VO, Si and SiO species, (b) is the magnified spectrum of SiO$_{2}$-, V$_{2}$O$_{3}$H$_{2}$O species and (c) and (d) are the overlay images of all the compounds present in the film. The spectra of ions with depth in figure 5(a) and their image overlays in figure 5(c) shows that vanadium oxides species dominate the film surface to ~500 s sputter time. This analysis is in good agreement with the above XPS results in that VO$_2$ (V$^{4+}$) and V$_2$O$_5$ (V$^{5+}$) and V$_6$O$_{13}$ which happen to be V$^{4+}$ and V$^{5+}$ mixed oxide. The TOF-SIMS spectrum in figure 5(a) and overlays images in figure 5(c) also made it possible to understand the V$_2$O$_5$ film layers in the SEM cross-section image in figure 3(b) and estimate the film thickness. It was found that in ~500 s sputter time ~30 nm vanadium oxides layer was sputtered completely and thereafter the gun penetrated into the interface region in ~700 s sputter time which is found to be rich in SiO$_2$. This SiO$_2$ layer has been estimated to be ~100 nm from the cross-section SEM image.

4.1. In situ Raman spectroscopy with gas sensing at 25 °C

Figure 6 shows the effect of atmosphere changes in the surface of V$_2$O$_5$ film when subjected to the effluent of NH$_3$ from the compound of ammonium acetate. Figure 6(a) illustrates the change in Raman spectra of the film when exposed to the molecule at different times (with intervals of 6 min) and to air (as a control spectrum) at 25 °C, while figure 6(b) represents the change in the Raman spectrum of the film when recovering from NH$_3$. In these profiles, the authors observed that the modes at low-frequency Raman line region of V$_2$O$_5$, earlier classified as rigid-layer modes [13] with bending vibration characteristics, were mostly unaltered in wavenumber when the film was subjected to the NH$_3$ effluent. Interestingly, the
one at 194 cm$^{-1}$ which shows a shift to low-frequency Raman line was observed to redshift. On the other hand, at the higher-frequency side of the Raman spectra, the 996 cm$^{-1}$ stretching mode displayed significant shift towards high frequency of the Raman line (blueshift) in all spectra (shown in figure 7(a)). The reverse effect was observed when recovering the film from effluent of NH$_3$ in figures 6(b) and 7(b), where both blueshifted 996 cm$^{-1}$ and redshifted 194 cm$^{-1}$ modes showed some recovery potential.

In accordance with equation (6) where the change in Raman line position $d\omega$, as a function of both elastic constant of the bonds, $\kappa$, and reduced mass of the atoms around these bonds, $\mu$, is given by $d\omega \propto d\kappa - (\kappa/\mu^2)d\mu$. In the present system case: $1/\mu = (1/m_O) + (1/m_V)$ or $\mu = m_Om_V/(m_O + m_V)$. The increase in $\kappa$ could be ascribed to acceptance of an electron by the V$_2$O$_5$ surface from the NH$_3$ effluent and vice versa, whereas an increase in $\mu$ could be ascribed to the acceptance of atoms from the gas by the V$_2$O$_5$ surface. Changes in $\kappa$ should be prevalent at 25 °C where adsorption is more likely to happen, while an increase in $\mu$ is likely to happen at high temperatures where chemisorption due to breakage of NH$_3$ bonds is preferred.

Since the 996 cm$^{-1}$ phonon is being blue-shifted [i.e. $d\omega > 0$] when exposed to NH$_3$, one expects that $d\kappa > d\mu/\mu^2$. This means that the change in elastic $\kappa$ is larger than the change in $\mu$. This suggests that V = O bond gains electrons from NH$_3$. On the other hand, the observation that the 194 cm$^{-1}$ phonon is being red-shifted when NH$_3$ is introduced means that $d\kappa < d\mu/\mu^2$. This could indicate that the V–O–V or O–V–O bonds prevalent in the VO$_2$ system are losing electrons to the NH$_3$ at 25 °C. This surprising result leads to the conclusion that bonds that have many electrons tend to gain more electrons whereas those bonds that have less electrons tend to lose even the few electrons that they have. This phenomenon is similar to an observation made during the halogenation of organic alkanes with HCl or HF or HBr in 1890s by a scientist known as Markovnikov, who observed that the H atom preferred to attach itself to carbon with the highest number of H atoms [31, 32].

A decrease in intensities of 145 cm$^{-1}$ low-frequency Raman line of V$_2$O$_5$ were also observed as a function of NH$_3$ effluent exposure (figure 6(a)) [33], but a reverse effect is observed when recovering the surface from NH$_3$ exposure in that the intensities increased slowly and saturate (figure 6(b)) with less potential when recovering from the NH$_3$ effluent. The profiles in figures 7(c) and (d) are representative of the change in intensity ($dI/I$) of the 145 cm$^{-1}$ Raman lines and wavenumber ($\omega$) peak-positions of 996 cm$^{-1}$ Raman line at 25 °C. These line profiles show that the intensities of 145 cm$^{-1}$ phonon
Figure 8. (a) Raman spectra at 100 °C of V2O5 film in air, and covered with NH3 molecule recorded at 6 min intervals, (b) Raman spectra at 100 °C of V2O5 film recovering from NH3 molecule recorded at 6 and 12 min intervals.

Figure 9. (a) Magnified images of 996 cm$^{-1}$ Raman lines when the film is exposed to NH3 at 100 °C, (b) magnified images of 996 cm$^{-1}$ Raman lines when the film is recovering from NH3 at 100 °C, (c) Gaussian fitted data of the heights of low-frequencies 143 cm$^{-1}$ Raman lines when the film is exposed to and recovering from NH3 at 100 °C, (d) Gaussian fitted data of peak-positions of high-frequencies 996 cm$^{-1}$ Raman lines when the film is exposed to and recovering from NH3 at 100 °C.
decrease and saturate with time during exposure, and experience difficulty in recovery due to the lack of vents in the homemade gas sensing cell shown in figure 1. This decrease in Raman scattered intensities in the presence of molecules may also be due to the absorption of laser light of free electrons created as a result of the interaction between V$_2$O$_5$ and NH$_3$ [10]. The Raman fingerprint position of 996 cm$^{-1}$ phonon recorded more significant blueshift (4 cm$^{-1}$) before saturation when exposed to the NH$_3$ molecule with relatively high potential of recovery than the redshift of the 194 cm$^{-1}$ (2 cm$^{-1}$) as shown in figure 7(d).

4.2. In situ Raman spectroscopy with gas sensing at 100 °C

In the same manner, figure 8(a) displays the Raman spectra of the film when exposed to the effluent of the NH$_3$ molecule at different times (with interval of 6 min) and to air (as control spectrum) at 100 °C, while figure 8(b) shows the change in Raman spectra of the film when recovering from the molecule. Figures 9(a) and (b) are the magnified spectra of 996 cm$^{-1}$ Raman lines when the surface is exposed to and recovering from NH$_3$ at 100 °C while the profiles in figures 9(c) and (d) are the change in intensity (dI/I) of 145 cm$^{-1}$ Raman line and wavenumber peak-position of 996 cm$^{-1}$ at 100 °C. The fact that the phonons are thermally mediated, coupled with the possibility of less scattering of light at the less-dense environment, may be responsible for the change observed at 100 °C relative to the effects observed in the case of room temperature measurements (25 °C). It is true that the way and manner in which the NH$_3$ molecule sits on the V$_2$O$_5$ will greatly influence the charge distribution between them [24]. In addition to the V$_2$O$_5$ crystal, geometrical structure and space group discussed in the introduction, V$_2$O$_5$ is a layered structure having distorted square pyramids of VO$_5$ which share edges and corners with the apex of the V–O configuration having a much shorter bond length compared to other bonds. This short bond length corresponds to a double bond attachment [17, 34]. One may propose that hydrogen atoms in an NH$_3$ molecule in a trigonal pyramid structure prefer to attach themselves to the vanadyl oxygen (i.e. the one with double bond and shorter length). If so, that may cause the molecule to give away some of their charges to the V = O layer and consequently increase the spring constant which leads to a blueshift in the Raman spectrum. Thus, the remnants of the NH$_3$ dissociation that are lying in the chamber may regroup and attach themselves to the bonded hydrogen atom and revert back to the NH$_3$ molecule when recovering V$_2$O$_5$ film from the coverage.

Other Raman frequency modes of V$_2$O$_5$ observed were 225, 270, 283, 305, 335, 406, 503, 614 and 700 cm$^{-1}$ at 25 °C and 100 °C, and they all belong to the vibration...
modes of V$_2$O$_5$ except the modes at 194 cm$^{-1}$ and 614 cm$^{-1}$ which are Raman fingerprint positions for the VO$_2$ structure [13, 19, 26, 35, 36]; this shows that VO$_2$ crystals are not participating in the reactivity of NH$_3$ effluent molecule.

4.3. Comparison of in situ Raman spectroscopy-gas-sensor tester and the traditional chemi-resistive gas-sensor testing station

Figure 10 shows electrical measurements of the V$_2$O$_5$ film in the presence and absence of NH$_3$ gas via the set-up described in the experimental section and previously reported [14, 37]. Figure 10(a) is the transient time-conductometric signals of the film when exposed to NH$_3$ gas at room (25 °C) and figure 10(b) is the signals at 100 °C. The profile shows a decrease in conduction of the film in the presence of NH$_3$ gas at 25 °C and 100 °C for every concentration. The sensor response and response time constant calculations for different concentrations of NH$_3$ gas are given as follows:

\[
\frac{i}{i_0} = \exp \left( \frac{t}{\tau_1} \right) \quad 0 \leq t \leq t_1 \quad (11)
\]

\[
\frac{i}{i_0} = \exp \left( \frac{t}{\tau_1} \right) \times \exp \left( \frac{t - t_1}{\tau_2} \right) \quad t_1 < t \leq t_2 \quad (12)
\]

where $i_0$ is the initial current of the sensor in synthetic air (flowing through the chamber), $t_1$ is the time for $i_0$ value, $i$ is either the current when the target gas is turned on or off and $t_2$ is the time at which the sensor recover to its original value. The quantity $\tau_1$ and $\tau_2$ are the time constants for response and recovery steps, these parameters were calculated by fitting the first order exponential function in equations (11) and (12). Figure 11(a) shows a response profile which was calculated from equation (11). The pattern shows better adsorption for all concentrations of NH$_3$ gas at 25 °C compared to the one at 100 °C. A response time constant plot was extracted from the same equation (11) as shown in figure 11(b). The response time constant in this paper is defined as the time it takes the sensor to reach 63% i.e 1 – $e^{-1}$ of its maximum after exposed to the gas [15, 38, 39]. This result also showed that the responses at 25 °C are faster than that of 100 °C but responses at 100 °C showed stability compared with ones at 25 °C. There is a cross-over in the response at 20ppm where the response time is found to be 50 s.

When one compares both the in situ Raman spectroscopy gas sensor tester and the traditional conductometric sensing as summerized in the table 1 below, firstly one can infer that at 25 °C the change in the wavenumber of 996 cm$^{-1}$ (with + shift or blue shift of 4 cm$^{-1}$) is greater than at 100 °C (with – shift or red shift of 3.2 cm$^{-1}$) and that the two temperatures showed significant and comparable recovery. On the other hand, the response according to the fractional change in intensity at 25 °C is great (with downward turn or –0.799) compared with the 0.419 of the chemi-resistive test and the one at 100 °C (with upward turn or +3.6) is large compared with the 0.222 of the chemiresistive test. This showed that the in situ Raman spectroscopy gas-sensor tester is more responsive than the chemiresistive sensor especially when considering the fact that the NH$_3$ effluent concentration in the chamber may be less or even far less than 40ppm. Also, when one compares the two response time constants, the chemiresistive sensor showed faster response compared with the in situ Raman spectroscopy gas-sensor tester. Again a low concentration of the effluent NH$_3$ in the in situ Raman gas sensing chamber may be the cause. This study shows that apart from using the response due to the fractional change in Raman intensity and chemi-resistive signal, Raman wavenumber (frequency) shift can be employed to selectively monitor gas leakages in the environment or to monitor decomposition of gases in industry during gas processing.

5. Conclusions

In summary, in situ Raman spectroscopy has been employed to monitor the reactivity of NH$_3$ effluence produced from ammonium acetate salt decomposed at 100 °C at the surface of 30 nm layers (with spherical particle of ~51 nm and pores of ~20nm) of V$_2$O$_5$ film deposited by PLD techniques. The results showed a recoverable red shift in the 194 cm$^{-1}$ phonons and blue shift in the 996 cm$^{-1}$ phonons upon the interaction of the molecule at ambient temperature (25 °C) and 100 °C. Adsorption effects (increase in intensity) of 145 cm$^{-1}$ phonons were also observed at these two temperatures. The Raman scattered adsorption effect has been explained using phonon confinement models by taking fractional change in intensity into account while the blue or red shift in the wavenumber (frequency) is related to the change in elastic constant and the reduced mass of the sensing surface in situ with NH$_3$ ambience. The adsorption effect is related to more and/or less Raman scattered photons.

<table>
<thead>
<tr>
<th>Table 1. Summary of Raman signatures versus chemi-resistive sensing of NH$_3$ molecule at the V$_2$O$_5$ surface.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temp °C</strong></td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>25</td>
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<table>
<thead>
<tr>
<th><strong>Temp °C</strong></th>
<th><strong>Chemiresistive at 40 ppm</strong></th>
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<tr>
<td>---------------------------------</td>
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<tr>
<td>25</td>
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</tr>
<tr>
<td>100</td>
<td>0.222</td>
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while frequency shift is explained as a decrease in the elastic constant (acceptance of charges from the molecule) when blue shifted and decrease in elastic constant (donation of charges) or increase in reduced mass (chemisorption) when red shifted. Acceptance of charges by the V$_2$O$_5$ surface from the molecule is observed to be prevalent at the ambient temperature while an increase in the reduced mass is observed at 100 °C. This is considered to be true since the breaking of chemical bonds or decomposition of NH$_3$ could only take place at a temperature higher than that of the ambient temperature.

Comparison and rankings of in situ Raman spectroscopy gas-sensor tester with the traditional chemi-resistive sensor tester showed that the in situ Raman spectroscopy sensor tester is excellent. Additionally, the significant recoverable tester showed that the gas-sensor tester with the traditional chemi-resistive sensor in situ XPS. This can be accomplished through (1) analysis of XPS same being donated to the V

$\text{O}^{+}$ bond leading to red-shift in the peak of the $\text{O}$ bond which shows a blue shift.

6. Future plans

The effect of electron capture from the V–O–V bond and the same being donated to the V = O bonds can also be seen with XPS. This can be accomplished through (1) analysis of XPS spectra or (2) in situ XPS with NH$_3$ gas injection. In (1) the analysis through peak deconvolution shows several chemical states of vanadium: V$^{4+}$ and V$^{5+}$ and oxygen: O$_2$– or O1s but that the three oxygen peaks (about 531, 533 and 535 eV) can be assigned to adsorbed oxygen (a), single bonded oxygen (b) and double bonded oxygen (c), respectively. It is more likely that upon NH$_3$ injection, the NH$_3$ and adsorbed oxygen interaction gives electrons to the double bond with a higher probability than to a single bond in the V$_2$O$_5$ chemical structure. This XPS explanation concurs very well with the experimental observation from our current Raman spectroscopy where we observe a relaxation of the V–O–V bond leading to red-shift in the peak and the stiffening of the V = O bond which shows a blue shift. As for (2), in order to verify the analysis in (1), there is a need to perform in situ XPS with a few ppm’s of NH$_3$ in the XPS chamber and monitoring the evolution of the V and O peaks. To perform such an experiment, one would need to incorporate a gas chamber to the XPS set-up. Currently we do not have XPS facility in our laboratory; the XPS data included in this manuscript was acquired from another institute.

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