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Page No.	CONTENT					
1 450 1100						
5	A real space approach to study the effect of disorder on the ±s-wave state of the iron-based superconductors.					
	In this work we present a real space based method to analyse the consequence of randomness on a model two band Hubbard Hamiltonian which represents a " \pm s-wave superconductor". A iron-pnictide superconductor has this symmetry of superconducting order parameter. Using our method we analyse the effect of substitutional disorder on diagonal and off-diagonal terms of the Hamiltonian of the system. Disorder in the interband intersite hopping integral is seen to kill superconductivity in the system. Thus such randomness leads us to a paradigm beyond Anderson's proposition for "dirty superconductors"					
	Subhadeep Bandyopadhyay, Prashant Singh and Shreemoyee Ganguly					
	On the size control of nanoparticles synthesis without chemicals					
10	Nanoparticles and subnanometer size particles of metal or semiconductor have a very important role in preventing environmental degradation which is alarming now a days. Threat to environmental damage can be averted by resorting to clean energy sources instead of conventional fossil fuel such petroleum, coal, etc., and controlling the toxic materials from spreading as well as reducing their life time by catalysing their degradation. Catalyzing energy conversion and degrading toxic materials is possible by the use of metal nanoparticles of specific size ranges. In this article, a novel method of production of nanoparticle with precise control on their size without the use of chemical reagents is briefly described.					
	Shyamal Mondal, Arpan Maiti and S. R. Bhattacharyya					
	Carbide fire in an acetylene gas plant – a case study					
14	This study deals with an incidence of small fire breaks in an industrial gas plant, manufacturing acetylene gas. It also explains the probable causes, preventive and corrective measures. What-if analysis and Cause-consequence analysis were used to identify the possible errors and the unsafe activities. Emergency procedures are also discussed. Finally some useful recommendations are listed which has been drawn for industrial facilities storing calcium carbide which is the raw material for acetylene production and preparing acetylene.					
	Gargi Bhattacharjee, Gopal Bera, Sudip Kumar Das, and Biswajit Singha					
	Perspectives of Quantitative Depth Profiling					
19	This article primarily deals with the compensation of 'matrix effect' in secondary ion mass spectrometry (SIMS) for direct quantitative analysis of materials using MCs^+ -SIMS approach. Emphasis has been given on exploring the formation mechanisms of MCs_n^+ (n = 1, 2,) molecular ions (M denotes the element to be analyzed and Cs^+ is the bombarding ion) emitted in the SIMS process. Following a brief introduction on SIMS, a study on MCs_n^+ molecular ions emitted from various metal and semiconductor targets under Cs^+ primary bombardment has been discussed.					
	Biswajit Saha and Rajiv K. Chouhan					
	Another New Family of Gold-Like Sequences					
24	In this correspondence, for a positive odd integer n, a new family U of binary sequences with $n+1$					
	$2^{n}+1$ sequences of length $2^{n} - 1$ taking three valued nontrivial correlations -1 and $-1 \pm 2^{\frac{n+1}{2}}$ is presented. This family U is consturcted using the families introduced by Boztas and Kumar, Kim and No. This family has the same correlation distribution as that of the well-known Gold sequences. So this family can be considered as another new class of Gold-like sequences.					
	Sankhadip Roy and Arnab Ganguly					

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In this work we present a real space based method to analyse the consequence of randomness on a model two band Hubbard Hamiltonian which represents a " \pm s-wave superconductor". A iron-pnictide superconductor has this symmetry of superconducting order parameter. Using our method we analyse the effect of substitutional disorder on diagonal and off-diagonal terms of the Hamiltonian of the system. Disorder in the interband intersite hopping integral is seen to kill superconductivity in the system. Thus such randomness leads us to a paradigm beyond Anderson's proposition for "dirty superconductors"

I. INTRODUCTION

The exploration of "unconventional superconductivity" (superconductivity whose microscopic origin can not be explained by BCS theory) in Fe-based superconductors was triggered by the discovery of $T_c=26$ K in LaFeAsO_{1-x} F_x (x=0.05-0.12) in 2008 [1]. Eventually the critical temperature could be raised to 56K (for Sm doped SrFeAsF) under high pressure [2]. The phase diagrams for certain systems like $Ba(Fe_{1-x}Co_x)_2As_2[3]$ or SmFeAsO_{1-x} $F_x[4, 5]$ shows the coexistence of long ranged magnetic order and superconductivity for a narrow concentration regime. Unlike cuprates, here atomic disorder in the superconducting Fe layer does not suppress superconductivity. But optimum T_c is obtained at concentration regimes where the magnetic order is destroyed. For certain other systems like $CeFeAsO_{1-x}F_x$ [6] superconducting order develops only at concentration regimes where magnetic order gets completely destroyed.

These systems have a discontinuous sign change of the order parameter (OP) phase between bands. This OP symmetry was analysed first for $LaFeAsO_{1-x}F_x$ compound by Mazin *et al* [7]. It is believed that superconductivity here is mediated by spin fluctuations (SF). SF can lead to triplet superconductivity or singlet one that changes sign over Fermi Surface. In order to satisfy the latter criteria it is not essential to have strong angular anisotropy of the OP (as is true for d-wave superconductors). It can be, and in this case it is satisfied by isotropic (s-wave type) pairing potential that has a sign reversal corresponding to the two Fermi Surfaces that participate in superconductivity. Although it is also multiband superconductivity, it is in principle different from that seen in MgB₂. Not only is the origin of Cooper pair formation different, but also the nature of the interaction. Here

the pairing interaction is repulsive, but pairing, due to the sign reversal of OP. Similar to d or p-wave pairing, here also the OP has a nearest neighbour intraorbital attractive pairing structure in real space, thus reducing the Coulomb repulsion between pairs. First principles calculations by Mazin et al [7]; Boeri et al [8]; Cao et al [9]; Ma et al [10] showed that Fe 3d orbitals contribute the major spectral weight near the Fermi Surface. The kspace picture reveals the presence of 2 hole circles around the Γ (0,0) point (involving Fe d_{xz} and d_{yz} bands) and 2 co-centered elliptical electron pockets around the M $(\pm \pi, \pm \pi)$ point (formed by hybridization of d_{xy} and d_{yz} bands). The fermiology in the said LaFeAsO_{1-x} F_x compound shows strong but broad AFM spin fluctuation near M point in the Brillouin zone. The said fluctuations though are too broad to cause a magnetic instability, are responsible for generating a superconducting state with OP of opposite signs on electron and hole pockets.

The pair potential for the hole band is provided by the electron band and vice versa for this system. Thus the band with larger DOS near the Fermi Level should interestingly govern the physics of the system but hold a smaller gap ! This indicates that the OPs, the critical temperature T_c and the response to disorder would be very unconventional indeed.

In order to model Fe-based superconductors, a study done by Bang *et al*[11] used a "phenomenological twoband model" for the system. To represent the appropriate physics in the simplistic possible way they used just one hole band around Γ and one electron band around M point. Here two kinds of OP symmetry leading to sign changing gaps between two bands is possible. One is the usual i) \pm s-wave symmetry and the other is the ii) double d-wave gap where each band has a d-wave gap but there is a π phase shift between two bands. Using similar parameters they showed that the \pm s-wave gap is energetically more favourable and thus more realizable in systems with FeAs-like gap.

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II. METHODOLOGY

A. Hubbard model for \pm s-wave

To analyse the consequence of randomness on a multiband \pm s-wave superconductor we look into the simplest model, namely, the two band percolating Cooper-pair in model system lattices. The corresponding Hamiltonian is:

$$\mathbf{H} = -\sum_{\langle i,j \rangle} \sum_{m,m',\sigma} t_{im,jm'} c^{\dagger}_{im\sigma} c_{jm'\sigma}$$
(1)
+
$$\sum_{i,m,\sigma} (\varepsilon_{im} - \mu) n_{im\sigma} - \sum_{\langle i,j \rangle,m} |U_{mm}(ij)| n_{im\uparrow} n_{jm\downarrow}$$

+
$$\sum_{i} \sum_{m,m',\sigma,\sigma'} |U_{mm'}(i)| c^{\dagger}_{im\sigma} c^{\dagger}_{im\sigma'} c_{im'\sigma} c_{im'\sigma'}$$

In Eqn.1 $c_{im\sigma}^{\dagger}$, $c_{im\sigma}$ are the electronic creation and annihilation operators for obrbital (band) m, with spin σ in site depicted by i of a two-dimensional (square) lattice. The index m runs over the two bands labeled by s and l, μ is the chemical potential and ε_{im} is the on-site energy at the site labeled by i in the band m. The hopping integral $t_{im,jm'}$ has four components:: a) $t_{is,js} = t_s$ is the hopping integral for s band from i to its nearest neighbour j, b) $t_{il,jl} = t_l$ is the hopping integral for l band from a site i to its nearest neighbour j. The interband hopping integrals are c) $t_{is,jl} = t_{sl}^{ij}$ is the hopping integral from a site i in the s band to one of its nearest neighbours j in the lband (or vice-versa) and d) $t_{is,il} = t_{sl}$ is the interband hopping integral.

Both intraband and interband interaction is included in our model Hamiltonian. It is to be noted that the interband interaction term is a pair tunneling term from the s-band to the l-band. The intraband interaction $[U_{mm'}(i)]$ is attractive and the interband interaction $[U_{mm'}(i)]$ is repulsive. The intraband interaction can be local or non-local (but not sign changing) leading to \pm s-wave superconductivity.

B. Treatment of disorder: Augmented space formalism

We shall mainly focus on the binary alloy kind of systems, where a randomness is present on the on-site energy term. This kind of disorder affects only the diagonal terms of the Hamiltonian. Let us think of a binary AB alloy, where A and B are the constituent atoms of the system with on-site energy ε_A and ε_B respectively. We also introduce a site occupation variable n_i which has the value either 0 or 1. If n_i is 1, then site will be occupied by A atom and if it is 0 then site will be occupied by B. So on-site energy of the system can be written as,

American Journal of Physical Sciences and Applications

$$\varepsilon_i = \varepsilon_A n_i + \varepsilon_B (1 - n_i)$$

= $\varepsilon_B + \delta \varepsilon n_i$ (2)

We shall define disorder strength D as, difference between on-site energy terms i.e $D = (\varepsilon_A - \varepsilon_B)$. Probability density of n_i for the system can be written as,

$$p(n_i) = x\delta(n_i - 1) + y\delta(n_i)$$
(3)

where x and y is the concentration of the A and B atom in the system respectively. Since n_i in this system has only two values so configuration space (ϕ_i) of n_i has rank 2. ϕ_i spanned by the states $|A_i\rangle$ and $|B_i\rangle$. In augmented space formalism we map every random variable n_i to a an operator \widetilde{N}_i such that \widetilde{N}_i acting with ϕ_i give probability density as its spectral density. Spectral density of the system is given by,

$$p(n_i) = -\frac{1}{\pi} \lim_{\eta \to 0} \Im \langle \emptyset_i \mid [(n_i + i\eta)\widetilde{I} - \widetilde{N}_i]^{-1} \mid \emptyset_i \rangle \qquad (4)$$

 \tilde{N}_i has the eigenvalues same as the eigenvalues taken randomly by n_i , corresponding to the eigenfunctions $|A_i\rangle$ and $|B_i\rangle$. Here $|\emptyset_i\rangle = \sqrt{x} |A_i\rangle + \sqrt{y} |B_i\rangle$, is known as average state. The state associates with one fluctuation at i^{th} site is given by, $|1_i\rangle = \sqrt{y}|A_i\rangle - \sqrt{x}|B_i\rangle$.

We can represent \widetilde{N}_i in the above basis as,

$$\widetilde{N}_i = x + (y - x)\gamma_i^{\dagger}\gamma_i + \sqrt{xy}(\gamma_i^{\dagger}\gamma_i)$$
(5)

$$\widetilde{\varepsilon} = <<\varepsilon_i>> +(y-x)\delta\varepsilon\gamma_i^{\dagger}\gamma_i + \sqrt{xy}\delta\varepsilon(\gamma_i^{\dagger}+\gamma_i) \quad (6)$$

This is the averaged on-site energy equation for random disorder in on-site energy.

Substituting the expression of \tilde{N}_i in equation(6) we get,

$$\widetilde{\varepsilon} = <<\varepsilon_i>> +(y-x)\delta\varepsilon\gamma_i^{\dagger}\gamma_i + \sqrt{xy}\delta\varepsilon(\gamma_i^{\dagger}+\gamma_i) \quad (7)$$

This is the averaged on-site energy equation for random disorder in on-site energy.

III. RESULTS AND DISCUSSIONS

A. Ordered Situation

Now, we will discuss the results on non-random twoband superconducting systems (for \pm s-wave) on square lattice with both intraband and interband Hubbard interaction. For all the calculations half filling of the states is maintained for particle-hole symmetry. Also we do not consider the interband intersite hopping term in this subsection. For our model Hamiltonian hopping integrals are chosen as: $t_s = 1.0$ and $t_l = 0.3$ for s- and l-band respectively for nearest neighbour. Inter band hopping is set to zero, i.e. $t_{sl} = 0.0$. Partial densities of states (PDOS) for sand l-band are shown in Fig. 1(a) for non-interacting case, i.e. $U_s = U_l = U_{sl} = 0$ for square lattice. The PDOS shows van Hove singularity in the band center, two flanking kink singularities and square root singularities at the band edges which matches with standard calculation using Blochs's theorem for ordered square lattice. Band width of the PDOS of s-band is wider because of bigger hopping amplitude.



FIG. 1: Study of superconductivity in an ordered square lattice (a) for non-interacting case, (b) for local \pm s-wave paring and (c) for non-local \pm s-wave pairing case.

We proceed to study the system when both intraband and interband interactions are present. Here intraband interactions can be local as well as non-local, attractive and fixed at $U_s = -3.5$ and $U_l = -3.5$. The interband interaction is local but nature of the interband interaction should be repulsive in order to observe \pm s-wave superconductivity. In Fig. 1(b) PDOS has been shown for $U_{sl} = 2.5$ where U_s and U_l are local. Superconduct-

American Journal of Physical Sciences and Applications

ing gap in both the bands signifies superconductivity for both the channel. This kind of superconductivity survives when the magnitude of intraband interctions are bigger than interband interaction. In Fig. 1(c) PDOS has been shown for $U_{sl} = 4.5$ where U_s and U_l are nonlocal. Here also superconductivity can be observed for both the channel. This kind of superconductivity survives even when the magnitude of intraband interctions are smaller than interband interaction.



FIG. 2: Variation of order parameter with magnitude of interband paring potential (a) for local \pm s-wave superconductor where interband interaction is repulsive, (b) for normal s-wave superconductor with attractive interband interaction

It will be interesting to study how OP behaves with interband interaction. Here intraband potential are set to $U_s = -3.5$, $U_l = -3.5$. Intraband interactions are restricted to be local. Now interband interaction potential U_{sl} is varied. Variation of the order parameter with the magnitude of U_{sl} has been shown in Fig. 2. U_{sl} is repulsive and attractive respectively for Fig. 2(a) and Fig. 2(b). When U_{sl} is repulsive, order parameter for s-band (Δ_s) and l-band (Δ_l) have opposite sign to each other but their magnitude increases with increase in magnitude of interaction potential U_{sl} . Both order parameter become positive when U_{sl} is switched to be attractive. For both the cases magnitude of (Δ_s) and (Δ_l) do not change.

B. Substitutionally Disordered Situation

We shall now consider two-band attractive Hubbard model for a binary substitutional alloy on a square lattice. Randomness in the onsite energy will be considered for s- or l-band, then we shall see how this randomness affect our system. We shall introduce randomness in our model Hamiltonian using Eqn. 6. Concentration is fixed at x = y = 0.5. To start with we shall discuss the effect of randomness for non-interacting case, .i.e. $U_s = U_l = U_{sl} = 0$. We keep the hopping integral $t_s = 1.0$ and $t_l = 0.3$ for the calculation. The disorder strength is defined as $D_m = |\varepsilon_m^A - \varepsilon_m^B|$, where m can be s- or l-band and $\varepsilon_m^A(\varepsilon_m^B)$ be the onsite energy for A(B) atom for a band m. PDOS of s- and l-band are shown in Figure 3(a) and Figure 3(b) respectively for different disorder strength. As disorder is increased we see the formation of a wedge in the PDOS corresponding to a split-band regime. Now we shall consider intercating case where all intercation potentials are set to non zero values.



FIG. 3: DOS for different values of disorder strength (a)and(b) for non-interacting *s*- and *l*-band. (c)and (d) for local \pm s-wave superconductor for *s*- and *l*-band. (e) and (f)for non-local \pm s-wave superconductor for *s*- and *l*-band

Here we set intraband interaction to $U_s = U_l = -3.5$, intraband interation potential is considered be local here. Interband interaction potential is set to be repulsive with $U_{sl} = 2.5$. PDOS for s- and l-band are shown in Fig. 3(c) and Fig. 3(d) respectively. Superconductivity survives with increasing disorder strength as OP reduces with increasing value of disorder strength. At higher disorder strength slight expansion of superconducting gap can be seen in l-DOS because of the split-band effect.

The effect of randomness of the interband intersite pairing amplitude t_{sl}^{ij} for systems with local +/- s-wave pairing is also studied. Here $U_s = U_l = -3.5$ (attractive) and $U_{sl} = 1.25$ (repulsive). The intraband inter site hopping amplitudes $t_s = 1.0$ and $t_l = 0.75$. In Fig 4 (a) $t_{sl}^{ij \ a} = t_{sl}^{ij \ b} = 0.9$ and $t_{sl}^{ij \ a} = 0.2$ in all the cases except for the D=0 case. In the D=0 case the system has no randomness. Here $t_{sl}^{ij \ a} = t_{sl}^{ij \ b} = t_{sl}^{ij \ ab} = 0.55$ so that the average value of t_{slij} is the same in all the cases. We see that when we put in randomness in t_{slij} and increase the diagonal disorder D after a certain point the gap in the DOS closes up just like when we put in diagonal disorder in a d-wave superconductor. In (b) we take a zoomed in view of this closing up of the gap with disorder. In (c) and (d) we have $t_{sl}^{ij \ a} = t_{sl}^{ij \ b} = 0.9$ and $t_{sl}^{ij \ ab} = 0.2$. So there is randomness in t_{sl}^{ij} . But here D=0.5, so we have not yet reached the limit where the system behaves like a d-wave superconductor with disorder. We keep the onsite interband hopping amplitude for A species (t_{sl}^a) fixed at 0.6 and vary t_{sl}^b from 0.1 to 0.6 . While decreasing randomness in t_{sl} tries to increase the order parameters, the increase in the resultant average t_{sl} tries to decrease the

order parameters Δ_s and Δ_l . So it is a competition between these two phenomenon that decides the behaviour of Δ_s and Δ_l .



FIG. 4: (a) DOS of a non-local \pm s-wave superconductor with random t_{sl}^{ij} , (b) zoomed view of the superconducting gap, (c) and (d) variation of order parameter for s- and l-band respectively with random t_{sl}^{ij}

IV. SUMMARY AND CONCLUSIONS

In the present communication we present a real space approach to analyse the consequence of substitutional disorder on a model multi band (orbital) superconducting system in real space. While the inter-orbital pairing is repulsive, the intra-orbital coupling is attractive. We have looked into what happens if the intra-orbital coupling is local and non-local (but without angular isotropy). For repulsive inter-orbital pairing there is a sign change of the order parameter phase between the bands which leads to pairing of electrons by pair tunneling phenomena. We have studied the effect of disorder in various situations. Randomness has been investigated in substitutionally disordered alloys where a) randomness is present only in the on-site energy (chemical disorder) and b) randomnes is present only in the hopping interactions. For ordered systems two gapped situation is got in the presence of interband pairing. Only in the case where intraband pairing potential is non local then superconductivity survives when the repulsive interband potential is stronger than the attractive intraband pairing potential. The gap in one of the bands in this case is determined by the hopping integral of the other band. While randomness in the on-site energy (chemical disorder depicted by disorder strength D as defined earlier) alone can not kill superconductivity in the system, a combined effect of randomness of the interband intersite pairing potential t_{sl}^{ij} and on-site energy kills superconductivity. Thus such disorder takes us to a regime beyond the validity of Anderson's theorem [12].

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On the size control of nanoparticles synthesis without chemicals

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Nanoparticles and subnanometer size particles of metal or semiconductor have a very important role in preventing environmental degradation which is alarming now a days. Threat to environmental damage can be averted by resorting to clean energy sources instead of conventional fossil fuel such petroleum, coal, etc., and controlling the toxic materials from spreading as well as reducing their life time by catalysing their degradation. Catalyzing energy conversion and degrading toxic materials is possible by the use of metal nanoparticles of specific size ranges. In this article, a novel method of production of nanoparticle with precise control on their size without the use of chemical reagents is briefly described.

I. INTRODUCTION

Under the tremendous pressure of developing human civilization, nature is at risk where life once was found and kept flourishing. With the increase in human comfort demand of energy has increased gigantically. Until recently, the main power source has been the fossil fuels and burning of which emitting harmful gases which are main reasons behind the global warming. Not only that, the pressure of human civilization giving birth many toxic chemicals, toxic dye being one them, harming the environment. There are enormous efforts being put to save the environment by scientists from a wide variety of disciplines in recent days.

Replacing the conventional fossil fuels in energy generation is one of those efforts. The most pervasive source of clean energy is solar energy, which falls on the earths surface with a daily insolation that is more than sufficient to meet global energy demand [1]. The technology for the conversion of solar to electrical energy using photovoltaic devices, such as silicon solar cells or dye-sensitised solar cells, is well-established. However, the generated electrical energy is not easily stored in large amounts, while solar energy is both diurnal and intermittent, and is least available when it is most needed, i.e. at night in winter. One strategy to overcome these issues is to develop a technology that generates a readily utilised chemical fuel directly from the solar insolation. In this regard, the most clean and viable solution is water, which can be broken into hydrogen and oxygen in the presence of sun light with the help of metal-oxide photoanodes in a photoelectrochemical (PEC) cell using a Pt counter electrode. The main challenge in all these possibilities is the efficient use of solar insolation which is found to be solved by the use of metal nanoparticles as photocatalysts or co-catalysts [2]. Role played by these metals in photocatalysis can be generally divided into: activity enhancement, photosensitization of semiconductors, solely localised surface plasmon resonance catalyst, photo-thermal effects, light trapping effect, etc. [2]

These activities are highly sensitive or crucially dependent on the nanoparticle size because optical absorption or scattering is highly size dependent e.g., in metal nanoparticles below a certain size absorption is dominating where as in metal nanoparticle above a certain size scattering is dominant [3].

II. CHALLENGES

Synthesis of metal nanoparticles with controlled size needs to be easy and very clean i.e., without a trace of residual chemicals which might affect the light interaction with nanoparticle. Size control also require very rigorous chemistry. Nanoparticles of metal can also be obtained by physical methods such as dewetting of thin films upon high temperature annealing, atomic layer deposition, magnetron sputtering at room or elevated temperatures. But in these processes of nanoparticle synthesis it is impossible to control size and number density simultaneously and the control in size is not so straight forward.

III. BREAKTHROUGH

Above mentioned difficulties of controlling size and number density of nanoparticles can be overcome if a synthesis scheme in physical method of deposition where nanoparticles can be produced first and then they can be filtered according to their sizes and then can be deposited with controlled deposition kinetic energy on any substrate. The scheme has been described in the Fig. 1. Fortunately, cluster beam deposition method [4] is a physical deposition method which can be performed in high vacuum condition and follows exactly the above mentioned steps. In the following sections the mechanism of production of size controlled nanoparticles in gas phase, before size selection or filtration and deposition, will be described. This process can be categorized as

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FIG. 1: A scheme for getting size selected deposition.

bottom up process where atoms are attached together to form clusters and then, through further growth, form nanoparticles. So the cluster production scheme is as follows: atom generation, nucleation and then aggregation or growth [5].

Atom generation Atom generation can be done in various ways e.g., thermal evaporation, ion sputtering, laser ablation, DC and RF magnetron sputtering, etc. In thermal evaporation heating of desired materials in crucible by resistive heating, electron beam induced heating are generally adopted. In ion beam sputtering highly energetic ions are used for striking out atoms from desired materials to get atoms. In laser ablation method high intensity laser is used to heat desired material to get desired atoms. For getting atomic vapour from wide range of materials from metals to insulators magnetron sputtering is best known so far.

Condensation In cluster production, the produced atomic vapour is condensed providing the desired condition to cool down the mixture of atomic vapour and the cooling gas. There are a few techniques to cool down the admixture e.g., low-pressure expansion through a nozzle called skimmer, collision by inert gas atoms. The area where this condensation takes place is known as the aggregation zone. In this zone, a supersaturated admixture is created in gas aggregation type source. Due to supersaturation of the atomic vapour small droplets are formed. These droplets are called nuclei. Through the growth of the nuclei in the aggregation zone clusters of different size are formed. The growth of clusters takes place through many possible mechanisms shown in Fig 2 and discussed below.

A. Atom attachment In this mechanism the nuclei collect more atoms on them to grow bigger forms clusters of different sizes. In this case atom attachment rate increases with size. Simply, this can be realized as $A_n + A \longrightarrow A_{n+1}$.

B. Coalescence Title and Author Details Two or more clusters when collide with each other in the gas





FIG. 2: Different schemes of cluster growth.

phase they stick and merges with each other to form larger cluster. This mechanism is called coalescence. This can expressed by the simple equation: $A_n + A_m \longrightarrow A_{n+m}$.

C. Ostwald ripening In this process formed clusters above a certain radius grows and at the cost of decay of some clusters less than that radius. This radius is called critical radius for cluster growth.

D. Aggregation In this process or mechanism clusters above a radius called critical radius for cluster coalescence do not merge completely when they come in contact with each other. In this mechanism of clustergrowth fractal type of structures are found to form.



FIG. 3: Schematic diagram of magnetron based cluster source.

As cluster production consists of different stages, according to the discussions in the previous sections, it is obvious that different experimental parameters might affect the generation and growth of cluster eventually affecting the final size distribution of the produced clusters. Different types of cluster sources have different control parameters so the control of size will also differ. Here, the whole discussion will be devoted to the magnetron based gas aggregation type cluster source [5]. In this type of cluster sources which is described in the Fig. 3 atomic vapour is generated by magnetron sputtering. In magnetron sputtering, a negatively biased magnetron target head, made with the desired cluster material, gets sputtered out by Ar ions. That atomic vapour along with the Ar and He gas makes a supersaturated mixtures in the water cooled aggregation zone. Thus, the parameters which governs the size of clusters are i) Ar gas flow, ii) He gas flow, iii) aggregation zone length, iv) Magnetron power, etc. To see the variation of cluster size distribution in the produced clusters mass spectra are generally analysed. Mass spectrum is the plot of intensity or number of a particular size of clusters in y-axis against the size or mass in the x-axis. In the Fig. 4, variation of mean cluster sizes with the different source parameters, as mentioned above, are plotted. It can be observed that mean cluster size is increasing with Ar flow initially, saturate at some value and then decreases. The nature of variation is like this because with the increase of Ar flow more atoms from the target are sputtered which in turn increase the probability of growth of clusters both in number and size. But probability of growth is also dependent on the dwell time in the aggregation zone. If Ar flow increase, that can sweep the clusters faster away from the aggregation zone depriving the clusters of the possibility of growth. That is why after a certain flow cluster size decreases. Following the same reason, with increase in He flow the mean cluster size is found to decrease and with increase in aggregation length mean cluster size increases at a rate more than a linear dependent one, as shown in the Fig 4. Fig 4 also shows an initial increase in mean clus-





FIG. 4: Size variation with different source parameters indicated in the x-axes.

ter size in the distribution with increase in magnetron power but after certain value the mean size decreases. Decrease in cluster size is associated with the increase in temperature in the aggregation zone due to increase in magnetron power. Thus mean cluster size and number of clusters produced can be controlled varying different suitable cluster source parameters. On the other hand it is clear that for any desired size we can choose the source parameters in such a way which can maximize the number of clusters or cluster-flux.

Doolr	Size	Magnetron	Agg.	Ar	He
(nm)	Size	power	Length	flow	flow
(IIIII)		(watt)	(mm)	(sccm)	(sccm)
1.3		11	4.8	10	60
1.5		11	4.8	15	60
1.65		11	14.8	15	60
1.75		11	14.8	15	40
1.82		11	24.8	15	60
2.00		11	54.8	15	60
2.25		26.9	34.8	15	60
2.5		26.9	104.8	15	40
2.75		40	104.8	15	20
3.0		55.6	104.8	15	15
3.25		98.7	104.8	17	10

TABLE I: Mean cluster size and corresponding required parameters.

Highly precise control in size can be achieved by this technique. And by size selection mechanism using quadrupole mass filter (QMF) further finer size control is possible before required deposition. Degree of fineness in size control can be estimated from the Table 1 where fine variation of mean cluster sizes have been shown which have been obtained through the proper choice of experimental parameters [6]. The control of size is evindenced from microscopy data in the mentioned reference where 1.5 nm, 2nm and 3.0 nm size clusters were actually deposited and observed the contribution in charge retaining capacity in MOS devices.

V. CONCLUSION

From the above discussion it is evident that a very good size controlled production of nanoparticles is possible by cluster beam deposition method using magnetron based gas aggregation type source. One control parameter controls size with different precision than others. For example change of helium-flow-rate changes the position of size distribution peak in finer steps than argon flow

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American Journal of Physical Sciences and Applications

rate. Change in aggregation length controls the peak position with bigger steps and so on. The process of size selected deposition is one step and do not require any rigorous knowledge of chemistry or use of chemicals. It should be noted that such a size control facilitate many applications which require stringent size control. There are enormous possibility in solar fuel generation where size controlled metal nanoclusters can be used as photocatalysts to efficiently convert solar energy as usable electrical and thermal energy. This technique, only, has the capability of controlling size and spatial density of deposited nanoparticles independently. The advantage is used in the work of Ref. [6].

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Carbide fire in an acetylene gas plant – a case study

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This study deals with an incidence of small fire breaks in an industrial gas plant, manufacturing acetylene gas. It also explains the probable causes, preventive and corrective measures. What – if analysis and Cause – consequence analysis were used to identify the possible errors and the unsafe activities. Emergency procedures are also discussed. Finally some useful recommendations are listed which has been drawn for industrial facilities storing calcium carbide which is the raw material for acetylene production and preparing acetylene.

I. INTRODUCTION

Calcium carbide primarily is an inert substance at dry atmosphere. But at wet atmosphere it reacts slowly with moisture to form acetylene, a highly inflammable gas and lime as per the reaction cited below, an exothermic reaction in nature, energy liberates about 1795.7 kJ/kg.

$$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2 \tag{1}$$

The rate of reaction is quite high in presence of water. Acetylene is a well known fuel gas used almost universally in gas welding. Acetylene is flammable and the National Electric Code (IS -2148: 2004) has a special designation for using electrical equipment in the acetylene users area. The mixture of air and acetylene is an explosive with explosive limit 2.5 - 82% by volume. Acetylene is approximately 10% heavier than air at 15° C.

The generation of acetylene from carbide is basically a simple process, but it was hazardous owing to high heat of reaction and explosiveness of acetylene in air. The conditions of Flammability (LEL %) 2.2 and (UEL %) 80 to 85 and the auto ignition temperature is 296° C. Pure acetylene can ignite by decomposition above 207kPa; therefore, the UEL is 100% if the ignition source is of sufficient intensity. A minor heat source like spark is good enough for catch fire and may cause an explosion from the bad to worse condition. Acetylene is chemically unstable and can decompose and release a large amount of energy, even in the absence of air or oxygen, if the cylinder is heated, struck or dropped. So it is imperative to follow the appropriate procedures for handling acetylene cylinder. Every day thousands of acetylene gas cylinders are used in the workplace. However, if the gas cylinders are not properly handled, the situation involved in a fire or explosion and makes the condition worse.

The accident of the acetylene user are very common particularly acetylene cylinder incidents. From 1^{st} January 2004 to 31^{st} December 2008 London

Fire Brigade Headquarters reported 471 cylinder incidents of which 91 involved acetylene cylinders (http://www.bcga.co.ukpreviewpdfs dated 09.03.2012). These accidents were due to either vibration of the cylinder or leakage from the cylinder. The leak from the acetylene cylinder may accumulate the gas prior to fire and explosion. The gas then mixed with ambient air within the room, forming a dangerous concentration of an ignitable mixture and results a high intensity fire (Koshy, 1999).

In general acetylene is not a serious toxic hazard, but it is a serious fire hazard and also an explosion hazard. Inhalation of acetylene is the only route of exposure. The exposure occur in the workplace where it is produced or used in wide range of industrial activities like chemical synthesis, welding etc. [NIOSH, 1976]. The toxic effect of acetylene exposure is asphyxiation as it displaces oxygen from air and causes in hypoxia. Exposure symptoms are dizziness, headache, fatigue, tachycardia, tachypnoea, nausea and vomiting. In severe cases convulsion, loss of consciousness and even death may occur (Williams and Whittington, 2001). Industrial acetylene often associated with toxic impurities like ammonia, arsine, hydrogen sulphide and phosphine and injury or deaths have been reported on exposure of industrial acetylene (NIOSH, 1976, Williams and Whittington, 2001).

The important task is to identify the real causes to minimize the incident. This study deals with a carbide fire incident in an acetylene manufacturing plant, its causes, preventive and corrective measures, emergency preparedness and useful recommendations which has been useful for the plant personnel.

II. EVENT LEADING TO THE OCCURRENCE

The incident took place in an industrial gas plant in West Bengal, India in one night of March 1993. The shift officer was on routine visit in the plant at around 11pm. It was a summer night and there was heavy downpour around for two hours from 8 to 10 pm. There was water logging in the factory roads due to rains. The shift offi-

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cer was on round by company car after the rain stopped. While passing beside the calcium carbide godown, heavy smoke was seen issuing from the entrance of the main godown. The officer then stopped the car on road and observed that smoke was issuing from a carbide drum. The drum was kept on floor outside the godown beside the covered walkway approaching acetylene gas generator room. No flame was found to come out of the drum. The drum lid was in open condition. The fire was extinguished by fire extinguisher immediately. There was no loss of life and no loss of property.

III. PROCESS OF FIRE IN THE PLANT

Water ingress to the carbide drum occurred during rain. Thus a typical carbide fire occurred as soon as carbide came in contact with water followed by formation of acetylene gas as result of temperature raised to the flash point of acetylene and there was auto ignition of acetylene.

IV. PROBABLE CAUSES OF THE INCIDENT

1. Carbide drum with dust and lump was kept for long time for necessary disposal, 2. Carbide dust was partially exposed to atmospheric air, 3. There was water ingress into exposed drum, 4. Formation of acetylene in the drum, 5. Auto ignition of acetylene inside the drum due to rise of temperature in drum, 6. Safe procedure was not followed for disposal of carbide dust and lump, 7. Strict supervision was lacking.

V. TYPES OF FIRE GENERALLY OCCUR IN ACETYLENE PLANT

There are primarily three types of fire that generally occur in an acetylene plant. They are as follows,

A. Chemical fire

Acetylene is a colourless and pungent gas, fire occurs for its flammable nature and high explosive limit in presence of air and oxygen in gas phase. Acetylene fire can occur at the following places during acetylene generation, i. Acetylene generator, ii. Acetylene gas holder, iii. Acetylene purifier, iv. Acetylene compressor, v. Acetylene cylinder filling manifold, vi. Acetylene cylinder yard. In all the above cases DCP (dry chemical powder) fire extinguisher and water are abundantly used as fire extinguisher.

American Journal of Physical Sciences and Applications

B. Acetone fire

Acetone is used in the acetylene cylinder where acetone initially absorbed by carbon (spongitype) particle and the filled acetylene in to the cylinder. One volume acetone can absorb 25 volume of acetylene. This measure is taken for safety reason. Acetone is a colourless volatile organic liquid. Acetone fire occurs for its flammable nature in presence of air and oxygen. Acetone fire can occur at the following places in a plant. i. Acetone storage area, ii. Empty acetylene cylinder. In both the cases fire is extinguished by foam (mechanical) fire extinguisher.

C. Calcium carbide fire

Calcium carbide is a solid material. Dry carbide is extremely inert, but carbide with moisture or water produce acetylene to cause carbide fire. This can happen at the following place in an acetylene producing unit- i. Calcium carbide godown, ii. Carbide charging device (skip hoist), iii. Acetylene generator hopper, iv. Acetylene generator water overflow line, v. Lime sludge pit. Carbide fire can only be extinguished by DCP (Dry Chemical Powder) only. Water should never be used for carbide fire since water with carbide produces acetylene that will augment the fire hazard to continue only.

D. Oil fire

Lubricating oil used in acetylene compressor. This is only occurring in acetylene compressor. The oil fire is always extinguished by foam (mechanical) fire extinguisher.

E. Electrical fire

This can happen at the following places in the acetylene plant, i. Carbide warehouse, ii. Electrical installations, e.g., compressor/pump motors, electrical panel, skip hoist motors, sludge water handling pump motor etc. Electrical fire always extinguished by carbon-di-oxide fire extinguisher, sand and also by DCP. Water is certainly not used for extinguishing electrical fire. The basic precaution for electrical hazard is to install flame proof electrical installations (IS 2148: 2004).

VI. ERRORS AND THE ACCIDENT ANALYSIS

The human error, unsafe act committed by the system operator which led to the accident. This unsafe act either involve doing something wrong or failing to do something. The maintenance failure is also a major cause of human errors. Table 1 shows what-if analysis and Fig.1

Sl. No.	What- if questions	Answer	Likely hood	Consequences	Recommendations
1.	If calcium carbide drums are in con- tact with moisture?	Acetylene formations occur.	Possible	Serious	Use local exhaust ventilation or work- ers should worn respirators and personal protective equipment (P.P.E.).
2.	If acetylene gas mix with air?	Explosions occur.	Possible	Serious	Establish an emer- gency response plan for responding in ac- cidental situation.
3.	If workers are illiter- ate or if operating procedures is not properly follow?	Accidents may occur.	Possible	Serious	General chemical and hazardous in- formation should be displayed to the workers and train them for proper handling calcium carbide.
4.	If the calcium carbide rules, 1987 are not properly maintain?	Typical carbide fires occur.	Possible	Serious	Follow the Calcium carbide Rules, 1987.
5.	If acetylene gas spread off-site?	Severely irritate and burn the eyes, skin, mouth, throat and shortness of breath.	Possible	Serious	On skin contact im- mediately wash or shower to remove the chemical, use P.P.E and goggles.
6.	If acetylene fire break down?	Explosion occur.	Possible	Serious	Establish an emer- gency response plan for responding in accidental situation and use explosion proof electrical equipment and fittings.

TABLE I: What-if analysis.

shows cause consequence analysis which reveals that the accident occurred due to maintenance and operating error. The management of the gas plant does not maintain the maintenance procedure of the carbide storage and the plant operators had insufficient knowledge as, i. The carbide drum which was necessary for disposal was kept for long time outside the godown on floor beside the walkway approaching acetylene gas generator room. ii. The lid of the drum was also in open condition. iii. The maintenance of the roof of walkway was very poor, so the water ingress to the carbide drums during rain due to spillage of rain water in the drum.

Thus the plant was running poor supervision. Although there was no loss of life and no loss of property

American Journal of Physical Sciences and Applications

but big incident could occur.

VII. RECOMMENDATIONS FOR CALCIUM CARBIDE STORAGE

Calcium carbide is a very water reactive chemical and it produce acetylene gas from calcium carbide and water reaction, so it should be stored in a proper way. License shall be required for storage of carbide and the following conditions must be followed, i. It shall be stored in a dry and well ventilated storage shed, which may form a part of or attached to a building provided that it is separated. ii. It shall be kept securely closed except while taking out carbide. iii. Observance of safety distance from the licensed storage shed necessary. iv. Not more than 1000 metric tonnes of carbide shall be stored in any one building, provided that not more than 250 metric tonnes of carbide is stored in any one room or other part of the building. v. A carbide storage shed may also form a part of, or attached to an acetylene plant provided that it is separated from other portions of the plant by substantial partition. vi. Every building storing carbide shall be surrounded by a wall or fence of at least 1.8 meters high to prevent unauthorized persons having access to the shed and are enclosed by such wall or fence shall cover the safety zone required to be kept clear. vii. Construction of storage premises - Every premises for storage of carbide shall be constructed of non-flammable material with cemented floor raised at least 30 centimeters from the surrounding ground level and be well ventilated. (Calcium Carbide Rules, 1987, Chapter Vstorage of carbide (http://explosives.nic.in/pdf/calciumgazette.PDF dated 03.01.09).

VIII. LESSONS LEARNT

1. Calcium carbide dust, sweeping, calcium carbide lump etc. should be disposed as soon as possible, 2. Carbide dust, lump etc. be stored at dry place before disposal, 3. Care must be taken for supervision of carbide handling and storage, 4. Refresher training programme to be in place in close frequency for all concerned, 5. Encourage good performance in maintenance work, 6. Good communications in maintenance team, working conditions (enough light, not very hot or not very cold, well ventilated clean storage area) are maintained by the management.

IX. CORRECTIVE ACTION

1. Training was conducted for all concerned responsible for acetylene plant operation, in regular interval of time, 2. Intense care was taken for carbide dust and lump disposal in the regular frequency, 3. Storing carbide outside carbide godown was bad practice, 4. Management should strictly follow the Calcium Carbide Rules, 1987, Chapter V for storage.

X. DISASTER MANAGEMENT

All the fire in acetylene plant hazards can lead to disaster within a short while in acetylene plant due to inflammable nature of acetylene. The acetylene plant must have a disaster management plan to meet emergency situation. A very short resume of disaster management plan is cited here. The salient features of the plan are as usual the following basic steps of a standard hazard management plan. They are as under, 1. Hazard identification,

American Journal of Physical Sciences and Applications

Safety audit, etc. 2. Hazard analysis / evaluation, HA-ZOP study etc. 3. Mitigation of hazard 4. On site / off site emergency plan 5. Rescue and evacuation 6. Public information 7. Roles and responsibilities of managerial and worker 8. Testing the plan

XI. RECOMMENDATIONS

1. Management must take the responsibility to train their personnel to be sure that they understand the hazards while handling flammable materials and training should be carried out in regular interval, 2. Carbide must always be stored and handled at dry and moisture free condition, as per calcium carbide rules, 1987, 3. Carbide must be used in the process on FIFO (First in First Out) principle, 4. Handle carbide/dust only with spark proof shovels. Disposal of carbide dust must be done in the open with copious supply of water as soon as possible, 5. System must be in place for periodic audit of operation and safety procedure of the plant by internal and external audit team, 6. At no condition acetylene release, leakage etc. can be allowed in an acetylene producing plants. All leaks to be identified and stopped with immediate effect. No delay is permissible, 7. All maintenance jobs must be done with best care and under permit of work procedure, 8. All operating staff must use Personnel Protective Equipments (PPEs), e.g., Air stream helmet, cotton suits, fire proof hand gloves, safety shoe while charging carbide to acetylene generator and other jobs to be performed with the recommended PPEs, 9. The alarm system should be provided in different work area to operate the plant safety, 10. All do's & don'ts must be displayed at the entrance and also important areas of the plant, 11. An emergency disaster management plan should be formulated the HAZOP study should be conducted to detect the human failure, if any, 12. The management is to manage available tools/equipment, reduce interruptions and distractions, housekeeping and tool control, manage fatigue-work schedules, manage boredom- by task assignment, appropriate rules procedures, reduce action slips, reduce memory lapses, improves task completion, improve attention and memory, reduces complacency and overconfidence, reduce risky decision making.

XII. CONCLUSION

The analysis of the incident has been carried out with respect to human errors (maintenance error). The "What-if analysis" questions were framed according to the working procedure, location, safeguards and "Causeconsequence analysis" was framed according to human error, maintenance error and inadequate atmosphere in the plant. Such methodical analysis helps to identify conditions that can lead to an accident or near miss situations. The carbide drum was for disposal kept for long time outside the godown on the floor beside the walkway



FIG. 1: Cause - consequence analysis.

approaching acetylene gas generator room; there was water ingress in to the drum during rain due to spillage of rain water from roof of walkway. Then a typical carbide fire occurred which came in contact with rain. The management of the gas plant does not maintain the maintenance procedure of the carbide storage according to Calcium Carbide Rules, 1987. The management should understand how to run the plant more safely and follow the suggested corrective actions and recommendations.

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Perspectives of Quantitative Depth Profiling

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This article primarily deals with the compensation of "matrix effect" in secondary ion mass spectrometry (SIMS) for direct quantitative analysis of materials using MCs^+ -SIMS approach. Emphasis has been given on exploring the formation mechanisms of MCs_n^+ (n = 1, 2,..) molecular ions (M denotes the element to be analyzed and Cs^+ is the bombarding ion) emitted in the SIMS process. Following a brief introduction on SIMS, a study on MCs_n^+ molecular ions emitted from various metal and semiconductor targets under Cs^+ primary bombardment has been discussed.

I. INTRODUCTION

The rapidly growing importance of advanced materials stems from the ever-increasing importance of thin films. For example, some fast developing areas are: thin film structures for microelectronics with tailored electrical properties, optical films with specific anti-reflecting and transparent properties, coatings and beam modified surfaces with high resistance to wear and corrosion etc. Controlled fabrication of these films requires a detailed and reliable, spatially-resolved chemical and structural analysis. In view of their planar structure, the analysis of in-depth distributions of chemical composition with high resolution is of primary importance, particularly near surfaces and interfaces. For this purpose, numerous methods have been developed during past five decades [1, 2]. Among these, micro-sectioning techniques based on sputtering in combination with surface analysis methods are most frequently applied [1-8] because they are applicable to practically any kind of materials and allow the attainment of optimum depth resolution (down to a few atomic monolayers) over a wide depth range up to several micrometers. There are many techniques available for performing an analysis of the elemental, chemical and physical makeup of a material. Many of these techniques are inexpensive to set up and operate, others are easy to interpret and some provide an absolute measurement capability. In short there is a large spectrum of techniques open to someone who wishes to do materials analysis of a sample. Each of these techniques has its own pros and cons and each its own niche. Conventional Ion Beam Analysis (IBA) techniques are far from the cheapest techniques to apply and can be complex to interpret. The scientific world has become more sensitive to costs and employing an expensive technique when a cheaper one would do is not a sustainable option.

Consequently, for IBA techniques to continue to be used at the forefront of research they must be seen to be providing something more than can be achieved via other methods. This might be in terms of the quality of the data, the speed of analysis (thereby effectively reducing the cost) or simply the only way to obtain a particular measurement.

Properties of material interfaces on atomic scale govern a great number of material properties and macroscopic phenomena. For example, structure and composition of surfaces (i.e. solid/vacuum interfaces) are responsible for all kinds of interaction of solids with ambient media as observed in adsorption, oxidation, corrosion, catalysis, friction and wear. Material properties such as brittle fracture, creep and re-crystallization are governed by the structure and composition of internal interfaces, for example, grain boundaries. In layered thin-film structures, the mechanical, thermal and chemical stability of interfaces between different materials (hetero-interfaces) is the way to reliable performance of many technological products such as microelectronic devices, sensors, components and protective coatings in various instruments, tools and medical prosthetics technologies. Despite the recent progress in interface science and technology, many details of the correlation between macroscopic physicochemical behaviour and microscopic property/composition/structure relationships of interfaces is not yet sufficiently well understood. The key to the study, control and optimization of interfacial properties appears to be a close link between the preparation and synthesis of interfaces and their chemical and structural characterization.

In particular, interfacial microchemistry is significant for the properties of interfaces [9]. The primary aim of the chemical analysis of interfaces is to determine their elemental composition and that of their surroundings with high spatial resolution, ultimately over atomic dimensions. Among the various techniques developed for this purpose, surface and interface analysis methods in combination with ion sputtering [5, 10-13] are most frequently applied because they are applicable to almost any kind of solid materials and allow the attainment of optimum depth resolution in the atomic monolayer region over a wide depth range up to several micrometres. In the context of sputter depth profiling, secondary-ion mass spectrometry (SIMS), secondary-neutrals mass spectrome-

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try (SNMS), glow discharge spectroscopy (GDS), Auger electron spectrometry (AES), x-ray photoelectron spectroscopy (XPS), ion scattering spectrometry (ISS) have always found their place among the most important methods for surface and interface analysis [1, 14].

Today, depth profiling using surface analysis methods in combination with ion sputtering has attained a high degree of maturity. Refinements of instruments and experimental techniques have led to great improvements in depth resolution. Instrumentation for depth profiling requires a source of energetic ions impinging on the sample surface and a suitable means of analysis of either the sputtered material or the residual surface after a certain sputtering time, as schematically depicted in Fig. 1. The ion source is usually an ion gun with beam raster facility, or low-pressure DC or RF plasma from which the ions are extracted. Analysing the sputtered particles (ions in Secondary Ion Mass Spectrometry (SIMS) or neutrals in Secondary Neutral Mass Spectrometry (SNMS)) in a mass analyzer during primary-ion bombardment yields direct information about the sample composition with depth. Alternatively, the optical emission of excited species can be determined by an optical spectrometer: Glow Discharge Optical Emission Spectroscopy (GDOES).

The complementary method is the analysis of the residual surface, for example, by electron or x-ray excitation and measurement of the secondary Auger- or photoelectron spectra with a charged-particle energy analyzer (AES and XPS). The latter can also be used for elemental analysis of the first surface layer by the determination of the primary ion energy loss due to surface scattering, as performed in Ion Scattering Spectroscopy (ISS). The basic procedure of depth profiling consists of recording the element specific peaks detected with the respective analyzer as a function of the sputtering time. For constant ion energy and beam current density the latter is proportional to the sputtered depth if the sputtering rate does not change with time.

Bombardment of a surface with energetic primary particles leads to surface erosion by emission of secondary particles from the sample. By continuous sputtering, layers beneath the original surface are subsequently exposed. Hence there are two ways to obtain the in-depth distribution of composition as a function of the sputtered depth: either by mass spectrometric analysis of the sputtered matter, as in SIMS and SNMS, or by chemical analysis of the remaining surface, as in AES, XPS and ISS in conjunction with sputter erosion of the material [2, 8]. These methods are markedly different with respect to elemental specificity and sensitivity, dynamic range, information depth etc. The sputtering process itself, however, is independent of the analysis method and should therefore be considered as a separate physical process.

Sputtering can be accomplished by removing atoms from the top monolayers of a solid [15, 16]. Therefore, a depth resolution in the monolayer regime should in principle be achievable. However, sputtering does not occur by an ideal layer by layer removal but is the result of a complex ion beam - sample interaction process. This process introduces a variety of distortional effects into the original morphology and composition of a sample, which are the cause of the much more extended profile broadening generally observed.

Recent progress in understanding the main physical processes and parameters involved in sputter erosion as well as its implications in specific surface analysis methods has led to a general framework of optimized profiling conditions for the achievement of high depth resolution. Glancing incidence of the ion beam (e.g. 80 to the normal to the sample surface) and low ion energy (< 1 keV)have pushed the depth resolution to its physical limits [6, 13, 17]. For this purpose low-energy (200 eV) ion guns with high current density have recently been developed [18]. Alternatively, molecular ions at higher energy can be applied because on impact the total energy is divided between the different atoms of the dissociating molecule [19], thus achieving a total depth resolution of 1.4 nm. In general, depth resolutions below 2 nm can now routinely be attained. In addition, the deconvolution of depth profiles by an experimentally determined resolution function is increasingly coming into use and enables us to reconstruct the original profiles with a precision of about one atomic monolayer [20-27]. Depth profiling is performed by ion bombardment of a selected area of a sample and subsequent analysis of a smaller area centred within the rastered area to avoid crater edge effects. A prerequisite for a meaningful in-depth analysis is a laterally homogeneous elemental distribution in planes parallel to the surface within the analyzed area. The experimental result consists of an elemental signal intensity as a function of the sputtering time (or the primary ion dose, in case of a calibrated ion beam current density).

In general, these raw data represent a more or less distorted image of the original, true in-depth distribution of composition. To obtain the latter, three fundamental tasks have to be solved [4-7]: (a) conversion of the sputtering time into depth, (b) conversion of the signal intensity from the surface compositional analysis method into concentration, and (c) assessment and correction of the shape distortions of a sputter profile, particularly near steep concentration gradients. These distortions limit the precision of a measured profile as described by the resolved depth, which is commonly identified as depth resolution z. These three problems are closely interlinked and can only be considered separately in a first order approximation.

II. SECONDARY ION MASS SPECTROMETRY

The fundamentals in Secondary ion mass spectrometry (SIMS) were laid by Herzog and Viehboeck (1949) [28]. Honig (1958) [29] constructed the first complete secondary ion mass spectrometer capable of sputter depth profiling. The first commercial SIMS for micro-analytical applications was introduced by Liebl (1967) [30]. Ap-



FIG. 1: Schematic showing instrumental parts and principal arrangement of a surface analysis instrument for sputter depth-profile analysis.

plications to semiconductor and thin-film analysis were shown by Werner (1968) [31] and depth profiling of thin surface layers was successfully demonstrated by Benninghoven (1969) [32] by the development of the static SIMS method.

Figure 2 shows the schematic representations of the technique. In this technique, the primary beam removes atomic layers of the sample at a rate determined by the intensity, mass and energy of the bombarding ions and by the physical and chemical characteristics of the sample itself. SIMS has evolved towards a cornerstone in many materials studies within the semiconductor community due to its excellent sensitivity, quantification accuracy and depth resolution. In recent years its application has expanded from simple, relatively deep dopant profiling in a single matrix towards the analysis of very shallow (i10 nm) profiles contained in complex structures and buried below (ultrathin) metallic films (which are used as gate or silicide material). These changes have increased the demand for SIMS with very high depth resolution considerably [33]. Moreover SIMS starts to be used to study the material interactions within these structures. Whereas the original quantitative success of SIMS was based on its use within the dilute limit i.e. the analysis of a minor (low level) constituent in a single matrix, the present applications have evolved towards the analysis of very high concentration levels and matrix compositions, thereby violating the basic assumptions put forward originally to quantify SIMS results accurately. Evidently, changes in ionization probabilities and sputter yields occur when going from one matrix to another one, thereby requiring complex data treatments and calibration procedures [34, 35]. Based on these observations it is clear that one needs to consider all the fundamental SIMS mechanisms contributing to the quantification, depth scale errors and depth resolution. The mechanisms underlying the potential errors can be identified by realizing that in addition to the desired process (i.e. the mass analysis of a sputtered, partially ionized, particle flux which can be converted into an intensity profile) concurrent processes occur. Indeed the energy deposition by the primary ion



FIG. 2: Schematic layout of secondary ion mass spectrometry.

leads to the development of a collision cascade which induces not only the sputter process but also causes at the same time many atomic displacements and thus a modification of the (instantaneous) internal profile.

Although the collision cascade is determined by the primary ion-matrix combination, the obtainable depth resolution for different elements is element specific [36]. This can be rationalized by considering the important mechanisms involved:

(1) The extent of the collision which determines the depth over which layers are intermixed. Obviously a larger mixing depth will mean a larger decay length. This mixing depth will scale with the primary ion energy (and penetration depth) leading to the universally observed scaling of the decay length with energy. (2) The amount of energy deposited within the collision cascade. Indeed when comparing similar penetration depths for different primary ions, these can only be achieved with higher/lower energy for the heavier/lighter ion. Hence, the energy deposition density and thus the number of displacements induced will be different. As long as the mixing has not yet led to a completely homogenized mixed layer, more displacements will imply longer decay lengths. (3) The energy transfer between a recoiling matrix element and the impurity and the distance traveled by this element for a given energy transfer. Both effects are element specific and cause the observed differences in decay lengths.

III. MATRIX EFFECT IN SECONDARY ION MASS SPECTROMETRY

Secondary emission of ions in the sputtering process is an inelastic phenomenon in ion surface interactions and has tremendous important applications in materials analysis. In SIMS [37], the ionized fraction of the sputtered species (known as secondary ions) is detected by a mass spectrometer equipped with appropriate ion collection optics. SIMS is sensitive to all elements in the periodic table, including hydrogen. Among all the surfaceanalytical tools currently available, dynamic SIMS is the most favoured technique because it offers in-depth (threedimensional) information with a combination of highest detection sensitivity (parts-per-billion) and excellent depth-resolution (down to less than 5 nm).

However, these advantages of SIMS are counterbalanced by its strong matrix effect [37, 38] i.e. the ionization probability of a given species varies by several orders of magnitude from one matrix to another, containing that particular species. Consequently, the secondary emission of a given ionic species is greatly affected by the instantaneous local surface chemistry of the sample. Since the ionization probability of a certain species is entirely matrix dependent, the secondary ion yield of that species has no straightforward relationship with the concentration of the species in the host, causing thereby a genuine hindrance to quantification. This phenomenon is known as the matrix effect in SIMS. Compensation of the matrix effect is needed for quantification in SIMS and is possible by several methods such as calibration curve [39], ion implantation standards [40] etc. All these approaches need standards with matrix composition close to that of the unknown sample. Moreover, it is very difficult to make compositional analysis of the interfacial regions using the above techniques. There is another technique known as infinite velocity approach [41], which makes use of the high energy part of the secondary ions that are essentially unaffected by the instantaneous local surface chemistry. The major difficulty in this method is, however, the detection of high-energy secondary ions because of their extremely low count-rates compared to that of low-energy secondary ions.

IV. ELEMENTAL QUANTIFICATION AND MCSN+ SIMS

Irrespective of the mechanism of secondary ion formation, quantification in dynamic SIMS is universally accepted as the conversion of a secondary ion current $I\pm$ The most widely used technique for quantitative SIMS analysis depends on finding relative sensitivity factors (RSF) for a certain species. In order to determine the sensitivity factors, appropriate reference materials or standards (the term is defined for materials whose composition has been determined by (t) of a given species in a homogeneous target matrix, measured as a function of time t, to a concentration C(z), measured as a function of depth z. Calibration of the depth scale is based on a strictly linear proportionality between the elapsed erosion time and the eroded depth of the sample, considering constant sputtering conditions throughout the measurement and consequently a fixed erosion rate. In reality, however, the linear time-to depth mapping may not be strictly valid as the erosion by ion bombardment introduces smearing of depth information by both target atom relocation and surface topography development. But the major factor that hinders elemental quantification is the matrix effect. However, there exit certain techniques through which one can quantify a species of

American Journal of Physical Sciences and Applications

interest in the host matrix.

The most widely used technique for quantitative SIMS analysis depends on finding relative sensitivity factors (RSF) for a certain species. In order to determine the sensitivity factors, appropriate reference materials or standards (the term is defined for materials whose composition has been determined by independent means, either directly by analytical measurement or indirectly from the method of synthesis) are needed. The accuracy of the quantification obviously cannot be better than that of the standards. However, in developing a suitable standard, the greatest problem encountered is often to get an independent, artifact-free reference method that can be used to calibrate the SIMS method. The principal characteristics of a suitable standard for the determination of sensitivity factors for SIMS are A. The composition should be homogeneous, both laterally and in depth since the sample layer eroded during determination of the intensity ratio may be quite shallow. It is also important to design the materials which allow the accurate measurement of erosion rates and the ion yields in the first few nm of a profile in order to establish the accuracy of the ultra-shallow profiling. B. The composition should not be significantly altered during analysis by the effect of ion bombardment.

There are two simple approaches towards quantification using standards the ion-implanted standards method.

A. Calibration curve method

This method relies on constructing a plot Ix, the intensity of the detected species as a function of Cx, the respective elemental concentration for standards containing the species x with various known concentrations [39, 42]. In order to keep the systematic uncertainties small, the sample to be measured must have a composition close to one of the standards used. The calibration curve of the species x in a matrix can be different from the calibration curve obtained for the same species in another matrix. For the determination of the unknown concentration of a species, the calibration curve is used as an analytical curve, where Cx is considered a function of Ix

B. Implantation standard method

This technique is much more accurate method for quantifying certain species present in a matrix [43,44]. In this method a local standard is prepared by implanting a controlled quantity of the species of interest with a known dose into a sample which should have the stoichiometry identical with that of the host matrix. By measuring the total fluence (dose) of the implanting species and the depth integral of the implant SIMS profile, RSF for the species x in the host sample is determined. The estimated (RSF)x is then used to get the instantaneous concentration of the species in the matrix. The use of implantation standards for SIMS was first reported by Gittins et. al. [45] and has proven extremely useful for quantitative SIMS analysis of electronic materials. Such standards provide quantitative information on both the local solute concentration and on the distribution of the solute in the structure. One of the great advantages of this method is that the constituent of interest can be implanted directly into the near-surface region of an unknown sample to fabricate an in situ standard. Since the implanted dose is sufficiently small in comparison to the atomic density of the sample, the response characteristics of the sample are not altered because of the presence of the implant. The implanted dose is, therefore, subjected to the same chemical environment as the sample atoms, and the matrix effects should be identical to both. Although quantification in a given matrix can be achieved by using standards with matrix composition as close as possible to the unknown sample, it is very complicated to quantify

or even interpret the analysis across interfaces composed of matrices of different nature like metal/semiconductor, metal/polymer, metal/ceramic, etc. Some attempts have been made to correct point by point distortion of a depth profile across an interface due to the matrix effect by using a calibration curve [46, 47]. This calibration curve giving the variation of ion yield with matrix composition was previously established by carefully studying a set of samples with different compositions. There is no doubt that the accuracy of the calibration was seriously limited by the exact evolution of the matrix composition at each point and the linearity of the calibration curve. SIMS analysis under conditions of reduced or no matrix effect is certainly a better way to measure the distribution of elements across interfaces. The matrix effect depends largely on experimental conditions, namely the nature of the primary ion, the incident angle, the detected species and the energy of secondary ions.

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Another New Family of Gold-Like Sequences

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In this correspondence, for a positive odd integer n, a new family \mathcal{U} of binary sequences with $2^n + 1$ sequences of length $2^n - 1$ taking three valued nontrivial correlations -1 and $-1 \pm 2^{\frac{n+1}{2}}$ is presented. This family \mathcal{U} is constructed using the families introduced by Boztas and Kumar[4], Kim and No [7]. This family has the same correlation distribution as that of the well-known Gold sequences. So this family can be considered as another new class of Gold-like sequences.

Keywords: Binary sequences, Quadratic Boolean functions, Correlation, Gold sequence, Gold-like sequence.

I. INTRODUCTION

Families of binary sequences with low correlation have important applications in code-division multiple access (CDMA), communication systems and cryptographic system([1],[2],[3]). Sidelnikov's bound([9]) is used to test the optimality of sequence families, which states that for any family of k binary sequences of period N, if $k \ge N$, then

$$R_{max} \ge (2N-2)^{\frac{1}{2}}$$

where R_{max} is the maximum magnitude of correlation values except for the in-phase autocorrelation value. The Gold's family ([5]) is the best known binary sequence family which satisfies Sidelnikov's bound. It has correlations $2^n - 1, -1, -1 \pm 2^{\frac{n+1}{2}}$, where n is odd. But the linear span of Gold sequences is too small to resist attacks based on Berlekamp-Massey algorithm. So the Gold-like families with larger linear span were constructed. The odd case of Gold-like sequence family was discovered by Boztas and Kumar^[4], whose correlations are identical to those of Gold sequences. For even n, Udaya[11] introduced families of binary sequences with correlations $2^{n} - 1, -1, -1 \pm 2^{\frac{n}{2}}, -1 \pm 2^{\frac{n}{2}+1}$ which corresponds to even case of Gold-like sequence family. Later Kim and No [7] further generalized the Gold-like sequences to GKW-like sequences by using the quadratic form technique and constructed families with correlations $2^{n}-1, -1, -1 \pm 2^{\frac{n+e}{2}}$ and $2^{n}-1, -1, -1 \pm 2^{\frac{n}{2}}, -1 \pm 2^{\frac{n}{2}+e}$ respectively, where n and e are positive integers, e|n.

In this correspondence, we introduce a generalized family of Gold-like sequences by combining the families introduced in [4] and [7]. This new family of optimal binary sequences with $2^n + 1$ sequences of length $2^n - 1$ has correlation distribution identical to that of Gold

sequence for odd n. So this family can be considered as a new generalized class of Gold-like sequences.

The remainder of the correspondence is organized as follows. In Section 2, we present the necessary preliminaries required for the subsequent sections and also discuss some known families of binary sequences with good correlations. In Section 3, we introduce the new family of binary sequences and our main result. In Section 4, we investigate the dimensions of the radicals of two quadratic forms. Finally in Section 5, we give the proof of our main result.

II. PRELIMINARIES

Let \mathbb{F}_{2^n} be the finite field with 2^n elements. Then the trace function from \mathbb{F}_{2^n} to \mathbb{F}_{2^m} is defined by

$$tr_m^n(x)=\sum_{i=0}^{\frac{n}{m}-1}x^{2^{mi}}$$

where $x \in \mathbb{F}_{2^n}$ and m|n. The trace function has the following properties:

- (i) $tr_m^n(ax + by) = atr_m^n(x) + btr_m^n(x)$, for all $a, b \in \mathbb{F}_{2^m}, x, y \in \mathbb{F}_{2^n}$;
- (ii) $tr_m^n(x^{2^m}) = tr_m^n(x)$, for all $x \in \mathbb{F}_{2^n}$.

Let f(x) be a function from \mathbb{F}_{2^n} to \mathbb{F}_2 and $\lambda \in F_{2^n}$. The trace transform $F(\lambda)$ of f(x) is defined by

$$F(\lambda) = \sum_{x \in \mathbb{F}_{2^n}} (-1)^{f(x) + tr_1^n(x\lambda)}.$$

Definition 1. Let $x = \sum_{i=1}^{n} x_i \alpha_i$, where $x_i \in \mathbb{F}_2$ and $\alpha_i, i = 1, 2, ..., n$, is a basis for \mathbb{F}_{2^n} over \mathbb{F}_2 . Then the function f(x) over \mathbb{F}_{2^n} to \mathbb{F}_2 is a quadratic form if it can be expressed as

$$f(x) = f(\sum_{i=1}^{n} x_i \alpha_i) = \sum_{i=1}^{n} \sum_{j=1}^{n} b_{i,j} x_i x_j,$$

where $b_{i,j} \in \mathbb{F}_{2^n}$.

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The quadratic form has been well analyzed in [8]. We also recall that the symplectic bilinear form of a quadratic form f(x) is

$$B(x,z) = f(x) + f(z) + f(x+z) \text{ for } x, z \in \mathbb{F}_{2^n}.$$

Finding the dimension of the radical of a quadratic form is very crucial for our result. The radical of the quadratic form f(x) is the number of sloutions of $x \in \mathbb{F}_{2^n}$ to

$$B(x,z) = f(x) + f(z) + f(x+z) = 0 \text{ for all } z \in \mathbb{F}_{2^n}.$$

The following lemma establishes the relation between the trace transform and the dimension of the radical of a quadratic form.

Lemma 1. (Helleseth and Kumar [6]) Let f(x) be a quadratic Boolean function on \mathbb{F}_{2^n} . If the rank of f(x) is 2h, $2 \leq 2h \leq n$, then the distribution of the trace transform values is given by

$$F(\lambda) = \begin{cases} 2^{n-h}, & 2^{2h-1} + 2^{h-1} times \\ 0, & 2^n - 2^{2h} times \\ -2^{n-h}, & 2^{2h-1} - 2^{h-1} times \end{cases}$$

where rank is the co-dimension of the radical of f(x).

All the sequence families considered in this paper are constructed by using the trace function $a(x) = tr_1^n(x)$ and some quadratic form b(x) as follows:

$$C = \{ f_i(x) | 0 \le i \le 2^n, x \in \mathbb{F}_{2^n}^* \}$$

where

$$f_i(x) = \begin{cases} a(v_i x) + b(x), & 0 \le i \le 2^n - 1\\ a(x), & i = 2^n. \end{cases}$$

and $\{v_0, v_1, \dots, v_{2^n-1}\}$ is an enumeration of the elements in \mathbb{F}_{2^n} .

The correlation function between two sequences defined by $f_i(x)$ and $f_j(x)$ can be given by the function from \mathbb{F}_{2^n} to the set of integers \mathbb{Z} as

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}^*} (-1)^{f_i(x) + f_j(\delta x)}$$

where $\delta \in \mathbb{F}_{2^n}^* = \mathbb{F}_{2^n} \setminus \{0\}$. $R_{i,j}(\delta)$ can be expressed as a trace transform

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}^*} (-1)^{tr_1^n([v_i + v_j]x) + g(x)}$$

= $-1 + \sum_{x \in \mathbb{F}_{2^n}} (-1)^{tr_1^n(x\lambda) + g(x)}$
= $-1 + G(\lambda)$

where $g(x) = b(\delta x) + b(x)$ and $\lambda = v_i + v_j \in \mathbb{F}_{2^n}$.

Definition 2. Let $\frac{n}{e} = m$ be odd. We define the boolean quadratic functions p(x) and q(x) by $p(x) = \sum_{l=1}^{\frac{n}{2}-1} tr_1^n(x^{2^{l+1}}), q(x) = \sum_{l=1}^{\frac{m}{2}-1} tr_1^n(x^{2^{el}+1}).$

Lemma 2. ([4]) The associated symplectic form of p(x) is

$$B(x,z) = p(x) + p(z) + p(x+z) = tr_1^n [z(tr_1^n(x) + x)].$$
(1)

Definition 3. (Boztas and Kumar [4]) For an odd integer $n = 2k + 1 \ge 3$, Boztas and Kumar introduced the following family G of Gold-like sequences

$$g_i(x) = \begin{cases} tr_1^n(v_i x) + p(x), & 0 \le i \le 2^n - 1\\ tr_1^n(x), & i = 2^n. \end{cases}$$

Theorem 1. (Boztas and Kumar [4]) For the family G, the distribution of correlation values is given as follows:

$$R_{i,j}(\delta) = \begin{cases} 2^n - 1, & 2^n + 1 \ times \\ -1, & 2^{3n-1} + 2^{2n} - 2^n - 2 \ times \\ -1 + 2^{k+1}, & 2^{2n-2}(2^{2k-1} + 2^{k-1}) \ times \\ -1 - 2^{k+1}, & 2^{2n-2}(2^{2k-1} - 2^{k-1}) \ times. \end{cases}$$

Lemma 3. ([7]) The associated symplectic form of q(x) is

$$B(x,z) = q(x) + q(z) + q(x+z) = tr_1^n [z(tr_e^n(x) + x)].$$
(2)

Definition 4. (Kim and No [7]) Let $\frac{n}{e} = m$ be an odd integer, where $m \geq 3$. Kim and No introduced the following sequences S which generalized the previous family

$$s_i(x) = \begin{cases} tr_1^n(v_i x) + q(x), & 0 \le i \le 2^n - 1\\ tr_1^n(x), & i = 2^n. \end{cases}$$

Theorem 2. (Kim and No [7]) For the family S, the distribution of correlation values is given as follows:

$$R_{i,j}(\delta) = \begin{cases} 2^n - 1, & 2^n + 1 \text{ times} \\ -1, & (2^n - 2^{n-e}) + 1)(2^{2n} - 2) \text{ times} \\ -1 + 2^{\frac{n+e}{2}}, & (2^{n-e-1} + 2^{\frac{n-e-2}{2}})(2^{2n} - 2) \text{ times} \\ -1 - 2^{\frac{n+e}{2}}, & (2^{n-e-1} - 2^{\frac{n-e-2}{2}})(2^{2n} - 2) \end{cases}$$

III. MAIN RESULT

In this paper we construct a family based on two quadratic forms $p(\lambda x)$ and $q(\zeta x)$ as follows.

Definition 5. Let $\frac{n}{e} = m \ge 3$ be odd. We define the family \mathfrak{U} of binary sequences by

$$u_i(x) = \begin{cases} tr_1^n(v_i x) + p(\lambda x) + q(\zeta x), & 0 \le i \le 2^n - 1\\ tr_1^n(x), & i = 2^n. \end{cases}$$

where e is also odd, $\lambda, \zeta \in \mathbb{F}_{2^e}$ and $\lambda \neq 0, \lambda \neq \zeta$.

For the correlation property of the family \mathcal{U} , we have the following main result.

Theorem 3. The family U has the following properties:

- 1. The maximal absolute value of the nontrivial correlation of family U is bounded by $R_{max} \leq 1 + 2^{\frac{n+1}{2}}$ and so the family is optimal with respect to Sidelnikov bound.
- 2. The correlation distribution is as follows:

$$R_{i,j}(\delta) = \begin{cases} 2^n - 1, & 2^n + 1 \ times \\ -1, & 2^{3n-1} + 2^{2n} - 2^n - 2 \ times \\ -1 + 2^{\frac{n+1}{2}}, & (2^{2n} - 2)(2^{n-2} + 2^{\frac{n-3}{2}})times \\ -1 - 2^{\frac{n+1}{2}}, & (2^{2n} - 2)(2^{n-2} - 2^{\frac{n-3}{2}})times. \end{cases}$$

IV. TWO QUADRATIC FORMS AND THEIR RANKS

A. Quadratic form $p(\lambda x) + q(\zeta x)$

From (1) and (2), the symplectic form of $p(\lambda x) + q(\zeta x)$ is

 $B(x,z) = tr_1^n [z(\lambda tr_1^n(\lambda x) + \zeta tr_e^n(\zeta x) + \lambda^2 x + \zeta^2 x)].$ Now for computing the rank of $p(\lambda x) + q(\zeta x)$, it suffices to find the number of solutions to

$$\lambda tr_1^n(\lambda x) + \zeta tr_e^n(\zeta x) + \lambda^2 x + \zeta^2 x = 0.$$

Let $tr_e^n(x) = a$. Then using the facts that $\zeta \in \mathbb{F}_{2^e}$ and $tr_1^n(x) = tr_1^e(tr_e^n(x))$, we get

$$x = \frac{\lambda t r_1^e(\lambda a) + \zeta^2 a}{\lambda^2 + \zeta^2},$$

which implies $x \in F_{2^e}$. Plugging into $tr_e^n(x) = a$, we get

$$a = \frac{\lambda t r_1^e(\lambda a) + \zeta^2 a}{\lambda^2 + \zeta^2},$$

which simplifies to $tr_1^e(\lambda a) = \lambda a$. So $a\lambda = 0$ or 1 which gives a = 0 or $\frac{1}{\lambda}$, only two solutions. That is, the rank of the quadratic form $p(\lambda x) + q(\zeta x)$ is 2h = n - 1.

B. Quadratic form $p(\lambda x) + q(\zeta x) + p(\delta \lambda x) + q(\delta \zeta x)$

Let $\delta \neq 1 \in F_{2^n}$ be a constant. From (1) and (2), the associated symplectic form is

$$B(x,z) = tr_1^n[z(\delta\lambda tr_1^n(\delta\lambda x) + \lambda tr_1^n(\lambda x) + \zeta\delta tr_e^n(\zeta\delta x) + \zeta tr_e^n(\zeta x) + (\lambda^2 + \zeta^2)(1 + \delta^2)x)].$$

So we need to count the solutions to $\delta\lambda tr_1^n(\delta\lambda x) + \lambda tr_1^n(\lambda x) + \zeta\delta tr_e^n(\zeta\delta x) + \zeta tr_e^n(\zeta x)$ $+ (\lambda^2 + \zeta^2)(1 + \delta^2)x = 0$. Let $tr_e^n(x) = a$ and $tr_e^n(\delta x) = b$. Then

$$x = \frac{\zeta^2 a + \lambda t r_1^e(\lambda a) + \delta(\zeta^2 b + \lambda t r_1^e(\lambda b))}{(\lambda^2 + \zeta^2)(1 + \delta^2)}.$$
 (3)

Let $X = tr_e^n(\frac{1}{1+\delta})$. So $tr_e^n(\frac{\delta}{1+\delta^2}) = tr_e^n(\frac{1}{1+\delta}) + tr_e^n(\frac{1}{1+\delta^2}) = X + X^2$ and $tr_e^n(\frac{\delta^2}{1+\delta^2}) = tr_e^n(\frac{1}{1+\delta^2}) = X^2 + 1$. Plugging (3) into $tr_e^n(x) = a$ and $tr_e^n(\delta x) = b$, and using the fact mentioned above, we have

$$(\zeta^2 a + \lambda t r_1^e(\lambda a) + \zeta^2 b + \lambda t r_1^e(\lambda b)) X^2 + (\zeta^2 b + \lambda t r_1^e(\lambda b)) X = a(\zeta^2 + \lambda^2),$$
(4)

$$(\zeta^2 a + \lambda t r_1^e(\lambda a) + \zeta^2 b + \lambda t r_1^e(\lambda b)) X^2 + (\zeta^2 a + \lambda t r_1^e(\lambda a)) X = \lambda^2 b + \lambda t r_1^e(\lambda b).$$
(5)

There are three cases.

ζ

1. If X = 0, then from (4) and (5), we have a = 0 and $tr_1^e(\lambda b) = \lambda b$ which gives $\lambda b = 0$ or 1. So we have only two solutions $(a, b) = (0, 0), (0, \frac{1}{\lambda})$.

2. If X = 1, then again we have two solutions $(a, b) = (0, 0), (0, \frac{1}{\lambda})$.

3. If $X = c \in \mathbb{F}_{2^e} \setminus \{0, 1\}$, then from (4) and (5), we get

$${}^{2}a + \lambda tr_{1}^{e}(\lambda a) + \zeta^{2}b + \lambda tr_{1}^{e}(\lambda b) = \frac{a(\zeta^{2} + \lambda^{2}) + \lambda^{2}b + \lambda tr_{1}^{e}(\lambda b)}{c}$$
(6)

Replacing $\zeta^2 a + \lambda t r_1^e(\lambda a) + \zeta^2 b + \lambda t r_1^e(\lambda b)$ in (4) and (5) with the right hand side of (6) and simplifying, we get

c(a+b) = a,

$$c((a+b)\lambda^2 + \lambda tr_1^e(\lambda b) + \lambda tr_1^e(\lambda a)) = \lambda^2 b + \lambda tr_1^e(\lambda b).$$

So we have four possibilities: **3.1** $tr_1^e(\lambda a) = 0$ and $tr_1^e(\lambda b) = 0$. Then

c(a+b) = ac(a+b) = b

So a = b = 0. **3.2** $tr_1^e(\lambda a) = 1$ and $tr_1^e(\lambda b) = 1$. Then

$$c(a+b) = a$$

$$c(a+b)\lambda = \lambda b + 1$$

and we have $a = \frac{c}{\lambda}$, $b = \frac{c+1}{\lambda}$ which lead to a contradiction as $tr_1^e(a\lambda) = tr_1^e(c)$ and $tr_1^e(b\lambda) = tr_1^e(c+1)$. **3.3** $tr_1^e(\lambda a) = 1$ and $tr_1^e(\lambda b) = 0$. Then

$$\begin{array}{rcl} c(a+b) &=& a \\ c((a+b)\lambda+1) &=& \lambda b \end{array}$$

and we have $a = \frac{c^2}{\lambda}, b = \frac{c^2+c}{\lambda}$. This is a solution if $tr_1^e(c) = 1$.

3.4 $tr_1^e(\lambda a) = 0$ and $tr_1^e(\lambda b) = 1$. Then

$$c(a+b) = a$$

$$c((a+b)\lambda + 1) = \lambda b + 1$$

and we have $a = \frac{c^2 + c}{\lambda}, b = \frac{c^2 + 1}{\lambda}$. This is a solution if $tr_1^e(c) = 0$.

Thus, for $X = c \in \mathbb{F}_{2^e} \setminus \{0, 1\}$, the associated symplectic form B(x, z) has

- 1. two solutions (a,b) = (0,0) and $(a,b) = (\frac{c^2}{\lambda}, \frac{c^2+c}{\lambda})$ when $tr_1^e(c) = 1$,
- 2. two solutions (a,b) = (0,0) and $(a,b) = (\frac{c^2+c}{\lambda}, \frac{c^2+1}{\lambda})$ when $tr_1^e(c) = 0$.

So the rank of $p(\lambda x) + q(\zeta x) + p(\delta \lambda x) + q(\delta \zeta x)$ is 2h = n - 1.

V. PROOF OF THEOREM 3

The proof can be divided into the following five cases. **Case 1:** $\delta = 1, i = j$: It is a trivial case and thus

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}^*} (-1)^{f_i(x) + f_i(x)} = 2^n - 1, \ 2^n + 1 \text{ times}$$

Case 2: $\delta \neq 1, i = j = 2^n$:

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2n}^*} (-1)^{tr_1^n(x) + tr_1^n(\delta x)} = \sum_{x \in \mathbb{F}_{2n}^*} (-1)^{tr_1^n([1+\delta]x)} = -1, \ 2^n - 2 \text{ times (number of choices for } \delta \neq 0, 1).$$

Case 3:
$$\delta = 1, i \neq j, 0 \le i, j \le 2^n - 1$$
:

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}^*} (-1)^{u_i(x) + u_j(x)}$$

=
$$\sum_{x \in \mathbb{F}_{2^n}^*} (-1)^{tr_1^n((v_i + v_j)x)}$$

=
$$-1, \qquad 2^n (2^n - 1) \text{ times}$$

Case 4: $i = 2^n, j \neq 2^n$ (or $j = 2^n, i \neq 2^n$): For fixed δ

$$R_{2^n,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}} (-1)^{tr_1^n([\delta+v_j]x) + p(\lambda x) + q(\zeta x)} - 1$$

From section 4, we know that the rank of the quadratic form $p(\lambda x) + q(\zeta x)$ is n - 1. So from Lemma 1, the distribution of correlations for fixed $\delta \in \mathbb{F}_{2^n}^*$ is

$$R_{2^{n},j}(\delta) = \begin{cases} -1, & 2^{n} - 2^{n-1} \text{ times} \\ -1 + 2^{\frac{n+1}{2}}, & 2^{n-2} + 2^{\frac{n-3}{2}} \text{ times} \\ -1 - 2^{\frac{n+1}{2}}, & 2^{n-2} - 2^{\frac{n-3}{2}} \text{ times}. \end{cases}$$

As δ varies over $\mathbb{F}_{2^n}^*$, the distribution becomes

$$R_{2^{n},j}(\delta) = \begin{cases} -1, & (2^{n}-2^{n-1})(2^{n}-1) \text{ times} \\ -1+2^{\frac{n+1}{2}}, & (2^{n-2}+2^{\frac{n-3}{2}})(2^{n}-1) \text{ times} \\ -1-2^{\frac{n+1}{2}}, & (2^{n-2}-2^{\frac{n-3}{2}})(2^{n}-1) \text{ times}. \end{cases}$$

Case 5: $\delta \in \mathbb{F}_{2^n} \setminus \{0, 1\}$ and $0 \le i, j \le 2^n - 1$: In this case, we have

$$R_{i,j}(\delta) = \sum_{x \in \mathbb{F}_{2^n}} (-1)^{tr_1^n([\delta v_i + v_j]x) + p(\lambda x) + q(\zeta x) + p(\delta \lambda x) + q(\delta \zeta x)} - 1$$

From section 5, we know the rank of the quadratic form $p(\lambda x) + q(\zeta x) + p(\delta \lambda x) + q(\delta \zeta x)$ is n - 1. So correlation distributions can be computed from Lemma 1 as

$$R_{i,j}(\delta) = \begin{cases} -1, & (2^n - 2^{n-1})2^n(2^n - 2) \text{ times} \\ -1 + 2^{\frac{n+1}{2}}, & (2^{n-2} + 2^{\frac{n-3}{2}}2^n(2^n - 2) \text{ times} \\ -1 - 2^{\frac{n+1}{2}}, & (2^{n-2} - 2^{\frac{n-3}{2}})2^n(2^n - 2) \text{ times}. \end{cases}$$

Combining the results of the above five cases, the distribution of the correlation values for the sequence family \mathcal{U} can be obtained.

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